OILY SLUDGE DEGRADATION STUDY UNDER ARID CONDITIONS USING A COMBINATION OF LANDFARM AND BIOREACTOR TECHNOLOGIES

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OILY SLUDGE DEGRADATION STUDY UNDER ARID CONDITIONS USING A COMBINATION OF LANDFARM AND BIOREACTOR TECHNOLOGIES

By

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ABSTRACT

Landfarming is one of the disposal methods used by oil companies to dispose of their generated oily sludge. Once in the soil, the sludge is subjected to biodegradation, leaching, and volatilization. Scientific studies to understand the degradation processes and to determine the degradation rate constants were mainly conducted in North American and European laboratories. However, no field studies were conducted in an arid region such as Saudi Arabia, the largest oil producer, where more than 30,000 m^3 of oily sludge is generated annually.

Field-scale research was conducted in the Juaymah area in the Eastern Province of Saudi Arabia to study the degradation of petroleum hydrocarbons under natural and enhanced conditions using landfarm and bioreactor technologies. The site was selected on the basis of its geographical location, site hydrology and climatic conditions. Based on factorial analysis, six landfarm and three bioreactor cells (2m x 2 m) were designed, constructed, and operated for one year starting September 2000 using sludge from an Arab Medium crude tank bottom. Sampling was carried out on a monthly basis and the analysis conducted at Saudi Aramco laboratories following the US EPA (United States Environmental Protection Agency) standard methods. The studied parameters included:

O&G (Oil and Grease), total hydrocarbon, BTEX (Benzene, Toluene, Ethyl benzene, and Xylene), pH, n-alkanes, microorganisms, metals, nutrients, and moisture content.

The results of this study revealed that weathering (evaporation) and not biodegradation was the dominant degradation mechanism. Of the three operating parameters (tilling, addition of water and/or addition of nutrients), tilling was the main parameter responsible for the highest percentage of reduction (76%) in the O&G concentrations. The addition of nutrients and water changed the soil properties and hence minimized the weathering effect. As demonstrated by the C_{17}/Pr and C_{18}/Ph ratios obtained from the GC-FID analysis, only those cells, which received nutrients showed evidence for biodegradation. In addition, a novel bacterial species known as *Burkholderia glumae* was identified, for the first time in Saudi Arabia, as one of the indigenous soil microorganisms responsible for the biodegradation.

The new analytical method of Open System Pyrolysis was used for the first time in this study and was compared with the routine O&G method to monitor oily sludge degradation. Although the results showed a similarity between these methods, however the Open System Pyrolysis provided a rapid method for the analysis of light volatile hydrocarbons in addition to several advantages over the O&G method.

A new model was developed to reflect a mirror image of the S-shaped curve of the collected data. The results obtained from this model exhibited a better fit (R^2) than the

zero-order, first-order and Monod kinetics models. The two-level factorial analysis (2^k) was used for the first time in this study to evaluate the significance of tilling, water, and nutrients to the overall degradation process.

The analytical results revealed that due to the method of air addition, the bioreactor system was not effective in achieving a high percentage of O&G reduction. The O&G reduction data indicates that natural attenuation should not be used as an on-going treatment/disposal method for oily sludges mainly because it is a very slow process.

The risk assessment revealed that landfarm activities pose a serious onsite risk particularly at the initial three-months loading period because of the presence of carcinogenic compounds such as benzene.

Recommendations for future research direction in the area of degradation under arid conditions are included in the thesis.

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List of Acronyms and Symbols

List of Acronyms

ANCOVA – Analysis of Covariance

ASTM- American Society for Testing Materials

BR – Bioreactor

BTEX – Benzene. Toluene. Ethylbenzene. and Xylene

GAB – General Aerobic Bacteria

HC - Hydrocarbons.

LF – Landfarm

LV - Light volatile components.

LV+TD+TC - Represents the total HC released between 180°C and 600°C.

O&G – Oil and Grease

OSHA – Occupational Health and Safety Administration

Ph – Phytane

PNA – Poly Nuclear Aromatics

ppm – Parts Per Million

Pr – Pristane

RBCA – Risk Based Corrective Action

SALAM – Saudi Aramco Laboratory Analytical Methods

SARA – Saturated hydrocarbons, aromatics hydrocarbons, resins, and asphaltene fractions

TC - Thermally crackable components.

TD - Thermally distillable components.

TH- Total Hydrocarbon

TKN – Total Kjedhal Nitrogen

T_{min} (°C) - Temperature at which HC volatilization is at a minimum.

TOC – Total Organic Compound

TPH – Total Petroleum Hydrocarbon

VOC – Volatile Organic Compound

List of Symbols

C = Exposed concentration, mg/m^3

CR = Contact rate, m^3/day

EF = Frequency of exposure, days/year

ED = Exposure duration, year

RR = Retention rate, dimensionless

ABS = Absorption into the bloodstream, dimensionless

BW = Average body weight, kg

AT = Averaging time, years

L = Length of the experiment cell, cm

H = Henry's law constant, cm3-water/cm3-air

d = depth of the contaminant zone, cm

ρ_s = Soil density, g/cm^3

U_{air} = Wind velocity, cm/s

δ_{air} = Air mixing height, cm

D_{eff} = Effective diffusivity, cm2/s

D_{air} = Contaminant diffusion in air, cm2/s

D_{wat} = Contaminant diffusion in water, cm2/s

θ_{as} = Air content in soil, cm3-air/cm3-soil

θ_{ws} = Water content in soil, cm3-water/cm3-soil

θ_T = Total porosity of the soil, dimensionless

τ = Averaging time for vapor flux, sec

k_s = Soil water sorption coefficient, g-water/g-soil

C_o = Concentration at initial time t_o, mg/kg

C_t = Concentration at time t, mg/kg

K_o = Zero-order rate constant

K_1 = First order rate constant, 1/day

μ_{max} = Maximum specific growth rate, day^{-1}

K_s = Half-velocity constant, mg/L

X = Concentration of biomass, mg/L

a = Constant, dimensionless

b = Constant, dimensionless

Max = Average concentration of first three observations, mg/kg

Min = Average concentration of last three observations, mg/kg

D = Max-Min, mg/kg

β_0 = Regression equation coefficient

β_1 = Regression equation coefficient

β_2 = Regression equation coefficient

β_3 = Regression equation coefficient

z = Constant, dimensionless

p = Probability, dimensionless

Chapter 1

Introduction

1.1 History of Landfarming

Landfarming, which is also referred to as land spreading, land application, sludge farming, land disposal, soil cultivation and land treatment (Huddleston 1979), is a managed technology that involves the controlled application of a waste on the soil surface and the incorporation of that waste into the upper soil zone (American Petroleum Institute 1983). This technology has been practiced by refineries since 1954 as a disposal method for their oily sludges (Grove 1978). During the 1970s when environmental concerns associated with uncontrolled disposal became apparent, and when environmental regulations were established and applied in North America and Europe (aimed at minimizing the risk of air and groundwater contamination), landfarming gained popularity. It became one of the most practiced and reported disposal methods for oily wastes in Canada, the United States (US), the United Kingdom, Denmark, Finland, France, Netherlands, Switzerland, and Sweden (Grove 1978; Beak Consultant 1981). By 1979, landfarming was the second most important disposal method used on a total dry weight basis among Canadian refineries, with landfilling being the first method (Beak

Consultant 1981). In the US. it became the most common method used by major oil companies to dispose of their generated oily sludge (Dotson et al. 1972; Dibble et al. 1979; Palis 1985). In 1983, it was estimated that at least one-third of all US refineries operated full-scale or pilot-scale landfarms (American Petroleum Institute 1983). Landfarming gained popularity over incineration, landfilling, and deep well injection due to the following distinct merits (Huddleston and Meyers 1979; Concawe 1980):

- Low energy consumption
- Low risk of pollution of the surface and groundwater due to the immobility of hydrocarbons or metals through the soil
- Minimal impact on the environment (good site appearance, absence of odors, etc.)
- Relatively low cost
- Compliance with sound industrial practices and/or government regulations
- Minimal residue disposal problems
- Compatibility of the technique with the climate, location and type of sludge treated

In 1984 this method lost its popularity when the United States Environmental Protection Agency (US EPA) issued the Land Disposal Restriction (LDR) as part of the Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA). This LDR, which was applied to landfarms, prohibited the land disposal of untreated hazardous waste. Landfarm operators had two options in order to operate their facilities: to treat their waste below the EPA specified contaminant levels (referred to as treatment standards), or to submit a petition demonstrating that there was no migration of

hazardous constituents from the injection zone (US EPA 2000). A no-migration zone is one from which there will be no migration of hazardous constituents for as long as the waste remains hazardous. Key issues for the no-migration test are air emissions, leachate infiltration into the groundwater, and the waste release through runoff into the surface water. As a result, most of the traditional landfarms in North America were closed.

In 1994, remediation by natural attenuation (RNA) of organic pollutants began to receive considerable attention. Natural attenuation is the reduction in mass, mobility, or toxicity of contaminants in soils, sediments, or groundwater by naturally occurring physical, chemical, or biological processes such as biodegradation, dilution, dispersion, adsorption, volatilization, and chemical stabilization (Swett et al. 1998). Several environmental regulatory agencies in the US have dedicated significant resources to developing guidance on implementing risk-based corrective action (RBCA) and RNA (ASTM 1994, 1998; US Air Force 1994, 1995; US EPA 1994, 1997). When examining the main processes under RNA, it is clear that RNA is similar to landfarming but it is being proposed as a remediation method rather than a disposal method. Landfarming appears to be returning as a major remediation technology. At the same time, ASTM, EPA and other agency guidelines have been used to calculate and interpret risks associated with petroleum release sites. These same guidelines are applicable to landfarms.

1.2 Oily Sludge

Oily sludge is one of the largest categories of wastes generated by the oil industry. Knowing the physicochemical characteristics of the oily sludge is important in

determining the fate of the sludge once it is disposed of and for evaluating the risks associated with the disposal mechanisms.

1.2.1 Composition of Crude Oil

Crude oil, as it comes out from the ground, contains organic and inorganic elements. The organic elements include mainly hydrogen, carbon, nitrogen, and oxygen; as hydrogen and carbon are the two major constituents, crude oil is referred to as hydrocarbon. On the average, petroleum contains about 85% carbon and 12.5% hydrogen (Neumann and Lahma 1981). The non-organic elements include heavy metals, sulfur, and sediments.

In a broader sense, petroleum hydrocarbons are divided into two main groups: aliphatics and aromatics. On a molecular level, the aliphatics and aromatics differ by the patterns of bonding between adjacent carbon atoms. Aliphatics are open chain hydrocarbons, and have three major subgroups: alkanes, alkenes and cycloalkanes. The simplest member of the aliphatic group is methane, which contains one carbon atom and four hydrogen atoms. The chemical formula of methane is CH_4. Aromatics are closed chain hydrocarbons that have six carbon membered rings. They are considered as unsaturated because their molecules do not contain the maximum potential number of hydrogen atoms. Aromatics are also divided into three major subgroups: monoaromatics, diaromatics and polynuclear aromatic hydrocarbons. The simplest member of the aromatic group is benzene, which has a chemical formula of C_6H_6. Figure 1.1 shows the petroleum hydrocarbon structural relationship (Potter and Simmons 1998).

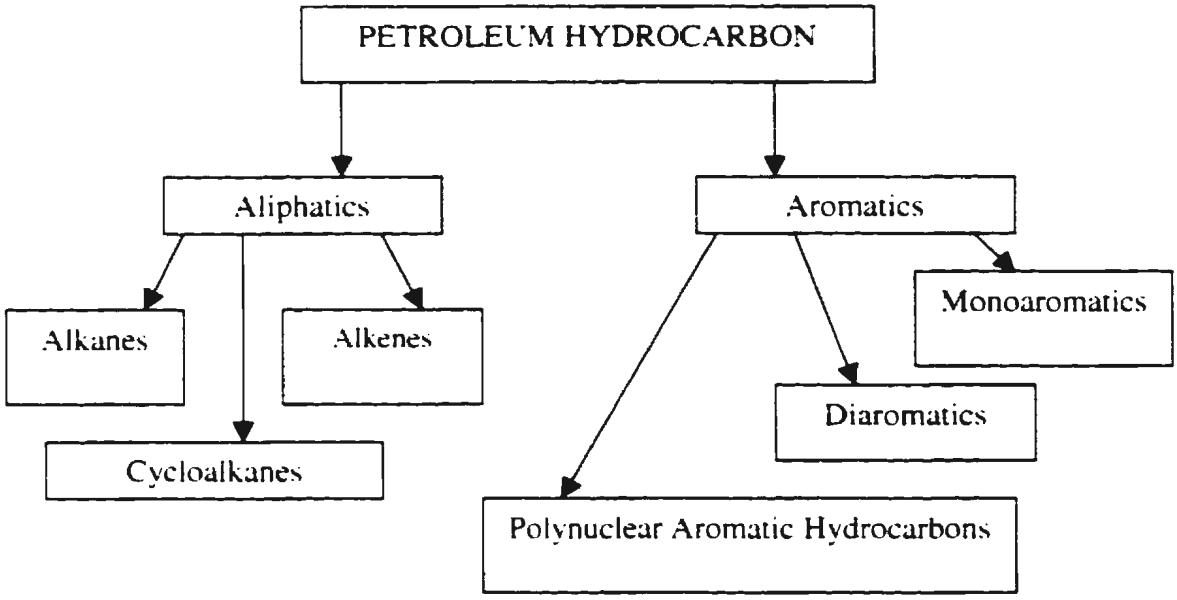

Figure 1.1 Petroleum hydrocarbon structure relationship
(modified from Potter and Simmons 1998)

1.2.2 Composition of Oily Sludge

Shailubhai (1986) stated that the major components of oily sludge include metallic and non-metallic compounds and water. The metallic constituents include zinc, chromium, nickel, vanadium, lead and copper; the non-metallic, n-alkanes, paraffin, olefins, aromatics, asphaltics, phenols and polynuclear aromatic hydrocarbons, and anions such as cyanide and fluoride. The composition of the sludge, Shailubhai noted, varies from batch to batch depending on the type of crude, the history of treatment, and the storage.

1.3 Risk Associated with Oily Sludge Disposal

Petroleum hydrocarbon constituents have been known to have an adverse impact on human health and the environment (Millner et al. 1992). The risk associated with oily sludge disposal in landfarms has not been reported in the literature. In order to determine

the risk associated with oily sludge in landfarms, a risk assessment process should be adopted. This process includes four major steps: hazard identification, exposure assessment, toxicity assessment, and risk characterization.

Total Petroleum Hydrocarbon (TPH) consists of thousands of compounds of which about 250 have been identified to date (Weisman 1998). To look at each of these 250 compounds individually in the oily sludge and to try to characterize the risk associated with each of them might be impossible. This has been realized by a group established in 1993 from more than 400 institutes, companies and agencies to address the large disparity between cleanup requirements used by different US states at sites contaminated with hydrocarbons. The group, Total Petroleum Hydrocarbon Criteria Working Group, identified 13 TPH constituents to be used to assess non-cancer risk, and benzene and carcinogenic polycyclic aromatic hydrocarbons (PAH) to be used as an indicator to evaluate cancer risk (Vorhees et al. 1999).

1.4 Landfarming in Saudi Arabia

Saudi Arabia, which is about one-third of the size of the USA, has the largest oil reserves in the world. It produces approximately eight million barrels of crude oil every day. With seven refineries, 22 bulk plants, several terminals and operating tank farms, oily sludge is one of the largest categories of generated industrial wastes. In a survey conducted by the Saudi Arabian National Oil Company (Saudi Aramco) in 1994, it was found that the oil industry generated approximately 30,000 cubic meters of oily sludge every year (Hejazi 1997). This study also found that the main source of the oily sludge was tank bottoms.

Other sources included API separator bottoms, operating slops, oil spills, operating residues and other miscellaneous sources.

Landfarming technology was introduced to Saudi Arabia in 1982. The decision to use this technology was based on information obtained through a review of technical documents (Watts et al. 1978; Phung et al. 1978; Bindra et al. 1979; Hejazi and Husain 2000). No scientific studies and/or research were conducted to support this decision. This was mainly due to several factors including the complexity involved in conducting such research, limited available experience, and the absence of environmental regulations. On the other hand, the arid environment that exists in Saudi Arabia, including the high temperature and the minimal rainfall (approximately 3.4 inches per year), made landfarming an attractive method. The first landfarm was constructed and operated in 1982. As of 2002, seven landfarms exist in Saudi Arabia with more under construction. Kuwait also used landfarming and other technologies to treat sites that were contaminated with oil as a result of the burning of Kuwait's oil wells during the Gulf War (Balba et al. 1998). In 1997, a Regional Refineries Waste Management Workshop took place in Abu Dhabi, the United Arab Emirates, to discuss the methods used for the disposal of refinery wastes. None of the papers presented at this workshop contained any scientific issues related to landfarming, even though this method was discussed (Gaocmao 1997). There are, however, several indications that the Gulf countries are moving in the direction of utilizing landfarming technology as the main method for treating their oily sludges.

1.5 Scope and Purpose of the Research

1.5.1 Research Goal

The primary goal of this research is to study the rates of degradation and to establish the mechanisms by which oily sludge is degraded under arid conditions.

This study was conducted through field experiments in Saudi Arabia, simulating the same conditions under which degradation processes occur in hot climates. The field study took 12 months to evaluate all of the parameters through a complete climatic cycle.

1.5.2 Research Objectives

Keeping in perspective the above goal, this research has the following objectives:

1. Study the kinetics of oily sludge degradation in landfarming under natural conditions, and under enhanced conditions with water, nutrients and tilling.
2. Study the kinetics of oily sludge degradation in a bioreactor (under controlled conditions).
3. Assess the effect of increasing oily waste loading under arid conditions.
4. Evaluate the effectiveness of combining both landfarming and a bioreactor for accelerating oily waste biodegradation rates.
5. Determine if biodegradation is the principal mechanism for the degradation of hydrocarbon versus weathering.
6. Assess the health risk associated with volatile organic compounds (VOC) emissions resulting from both landfarm and bioreactor operations for onsite workers.

Chapter 2

Literature Review

2.1 Introduction

Most of the research conducted to understand the mechanisms of landfarming processes was done prior to the issuing of the Land Disposal Restriction rule in 1984. The main focus of these studies was to generate information that could be used in operating landfarms. A report prepared by the American Petroleum Institute (1983) described the design, operation, and performance of land treatment systems in the petroleum industry. This report was used as a reference guideline by regulatory agency permits writers, petroleum industry personnel and others interested in assessing the performance, design, operation, and monitoring of land treatment systems. Concawe (1980) issued a report entitled "Sludge Farming: A Technique for the Disposal of Oily Wastes" which was intended to outline the scope of the landfarming method and its application, with a brief process description, sampling and analytical procedures and the results of experiments conducted in Europe and North America. The Landspreading of Sludges at Canadian Petroleum Facilities report, prepared for the Petroleum Association for Conservation of the Canadian Environment (Beak Consultant 1981), provided scientific and practical

information to assist proponents and operators of landfarms. In addition, most of the oil companies that operate landfarms have developed operating procedures based on conventional agricultural methods with negligible consideration of the scientific processes involved (Beak Consultant 1981; Arabian American Oil Company 1984). These procedures contained information that was of an operational nature: site selection (soils, hydrological, climatic considerations), rate of applying sludges, water and nutrient requirements, the need to adjust the pH of the sludge, tilling frequency and monitoring parameters.

In recent years, more emphasis has been placed on conducting field studies on natural attenuation as a disposal method for industrial wastes. The principle of landfarming is the same as that of natural attenuation. Buchanan and Sehayek (1999) reported that in 1998 the Interstate Technology Regulatory Cooperative (ITRC), a group of 30 states working together to foster the use of innovative remediation technologies, and the Research Technology Development Forum (RTDF), a joint government/industry group dedicated to developing and applying innovative remediation technology in the US and Europe, joined together and employed a multidisciplinary approach to demonstrate such innovative remedial technologies in the field. All of this work took place in the US and European countries with no attempt to do similar work in countries with arid climates such as Saudi Arabia. An in-depth evaluation of the three main factors that should be considered to determine the effectiveness of landfarming (soil characteristics, sludge characteristics, and climate conditions) has not been conducted. Therefore, due to the

distinctly differing climatic conditions the information available from US and European landfarming practices cannot be applied in an arid region like Saudi Arabia.

The process of landfarming encompasses many scientific disciplines including soil mechanics, hydrology, chemistry, and microbiology. Soil plays one of the most important roles in this technology as it provides the required media that influences the fate of hydrocarbons. On the other hand, the hydrology of the site dictates the location of the landfarms. Chemical reactions govern the processes that occur between the soil and the hydrocarbons (adsorption, leaching, volatilization, oxidation, etc.). Microbial assimilation is the principal means of hydrocarbon degradation (Arora et al. 1982).

The majority of the literature produced on landfarming can be classified into the following subject categories: 1) landfarming methodology, 2) scientific explanation of landfarming processes, 3) parameters influencing the performance of landfarming processes, and 4) the use of bioreactor technology to enhance landfarming processes.

2.2 Landfarming Methodology

The fundamental concept of the landfarming technique is well defined in the literature. The US EPA (1998) stated that this method is based on spreading the oily sludge in a thin layer on the ground surface and stimulating aerobic microbial activity within the soil through aeration and/or the addition of minerals, nutrients, and moisture. The enhanced microbial activities result in the degradation of adsorbed petroleum product constituents through microbial respiration. Bindra and Zestar (1979) defined landfarming as the

application and biodegradation of oily wastes on soil in a controlled and monitored environment. They stated that oily sludge should be uniformly deposited and mixed with the top six to nine inches of soil so that the natural soil microorganisms will biologically degrade the waste oil. Grove (1978) explained the biodegradation of oily sludges (commonly called landfarming) as the repeated application of an oily sludge to a given soil and the controlled promotion of naturally occurring microbial assimilation, which converts the hydrocarbons to the end products of CO_2, and H_2O, and increases the humus content of the soil. Concawe (1980) described landfarming as a destructive technique based on the biological oxidation of hydrocarbons by natural soil microflora. The Texas Department of Water Resources (1976) described landfarming as a waste management practice where waste materials are mixed or applied to the land surface. They further said that landfarming utilizes the physical, chemical, and biological capabilities of the soil-plant system to serve as an ultimate receiver of wastes and inactive contaminants. The American Petroleum Institute (1983) noted that most of the biodegradation process takes place at the surface soil layer (0.5-1.0 ft) and called this layer the *zone of incorporation*. They also stated that since additional treatment and immobilization of the waste could occur up to a depth of 5 feet from the surface, this layer, known as the *treatment zone*, needed to be monitored. Finally, they stated that soil conditions below 5 feet are not favorable because oxidation will not take place. Figure 2.1 illustrates the zones of interest in landfarms.

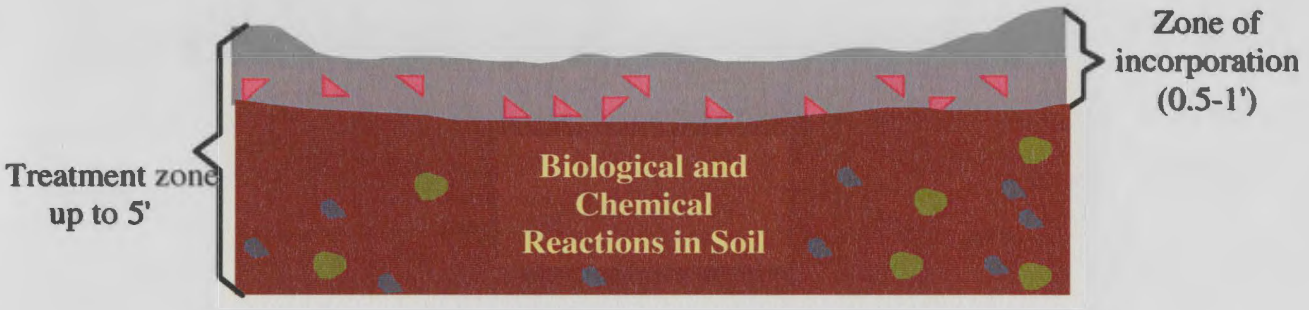

Figure 2.1 Landfarming methodology
(American Petroleum Institute 1983)

2.3 Landfarming Processes

The fate of oily sludge "once it is incorporated into the soil matrix" is subject to many processes. Huddleston (1979), in an attempt to explain the fate of oily sludge in the soil, stated that wastes added to the soil environment are subject to one or more of the following processes: biodegradation (decomposition), leaching of water-soluble components, incorporation into the soil matrix (adsorption), and volatilization. Figure 2.2 illustrates the fate of waste in the landfarming process.

Biodegradation is the principal method of hydrocarbon degradation in landfarms where the biological oxidation of hydrocarbons by natural soil microflora occurs. Microorganisms utilize the hydrocarbons as a source of food and energy by breaking them down into forms required by higher forms of life (Raymond et al. 1976; Grove 1978; Huddleston and Meyers 1979; Concawe 1980; Beak Consultant 1981; American Petroleum Institute 1983; Madsen 1991). The soil microorganisms degrade the oily sludge into intermediate products such as alcohols, phenols, esters, aldehydes, ketones, and carboxylic acids. These intermediate products are ultimately converted to carbon

dioxide, water and biomass (Arora et al. 1982). The biodegradation process differs from other landfarming processes in that it alters or destroys the contamination by transforming it into carbon dioxide, water and other non-toxic compounds, while the other processes reduce the concentration or the mobility of contaminants without destroying them (Grove 1978; Arora et al. 1982; Shailubhai 1986; Swett et al. 1998). The oxidation of oil can be represented by the following equation:

$$\text{Oily sludge} + \text{Bacteria} + O_2 \longrightarrow CO_2 + H_2O + \text{Biomass}$$

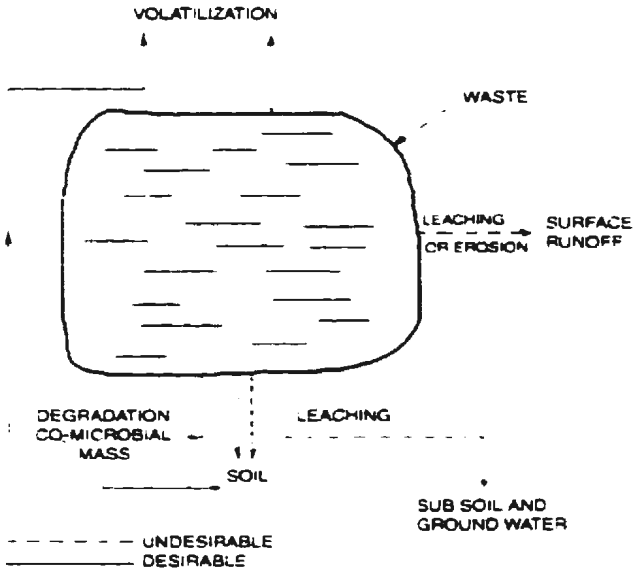

Figure 2.2 Fate of landfarming oily wastes (Huddleston 1979)

Despite biodegradation being the principal process for hydrocarbon degradation, it has not been fully studied from a scientific point of view, and many of its components are still not well explained. Block et al. (1993) stated that much of the recent data on biodegradation lie in the hands of bioremediation process developers and contractors and

that they should be contacted if the literature data are insufficient to evaluate the feasibility of treating a particular contaminant. In the Canadian National Contaminated Sites Remediation Program, McNicoll and Baweja (1995) stated that few, if any, studies have tried to quantify the amount of volatilization and biological degradation that occur when the landfarming method is used.

Bossert et al. (1984) conducted a laboratory experiment to determine the fate of Poly Nuclear Aromatics (PNAs) and total hydrocarbon in the soil during the active and closure periods of landfarms. Seven loads of oily sludge from a Dissolved Air Flotation (DAF) unit were used and monitored for 1280 days. The results showed that mineralization (conversion of hydrocarbons to CO_2) was the major route of hydrocarbon disappearance during the active period, while humification (incorporation of hydrocarbons into soil organic matter) was the main route of hydrocarbon disappearance during the closure period. The results also showed that in the sludge, the predominant PNAs were degraded more completely (85%) than total hydrocarbons (47%) and that substantial amounts of non-degraded hydrocarbon remained at the end of the study. All of these findings were obtained from laboratory tests. Actual field studies to give firm conclusions were not conducted. Such studies are needed to support any of these findings, to clarify which components biodegrade faster, and look at other hydrocarbon components of interest such as BTEX (Benzene, Toluene, Ethylbenzene and Xylene).

Block et al. (1993), during his evaluation of the biodegradation process, stated that while most petroleum constituents are biodegradable, the rate of biodegradation could vary

dramatically. This will depend on hydrocarbon composition, climate, site conditions, etc. Varying conditions from one area to another and their effect on the biodegradation rate of hydrocarbons were stressed in this study. Block also noted that bioremediation as a technology has been successfully applied at many sites; however, in a few cases, it did not work. In one case bioremediation technology was not effective in treating soil contaminated with diesel fuel, even though it was very successful in treating soils contaminated with similar diesel fuel at other sites. Block also mentioned cases where bioremediation treatability testing was successfully conducted in the laboratory but did not work in the field: "Yet even after successful treatability testing, the lack of biological degradation in some cases was still puzzling". Block concluded that many variables influence biodegradation processes. In the case of diesel fuel, the source of crude oil, refinery capabilities and the blend of streams generated from crude distillation and downstream processing will affect biodegradation and one refinery's diesel may biodegrade in a significantly different manner than others. Shailubhai (1986) concluded that under laboratory conditions, it has not been proven possible to degrade oily sludge completely. Although landfarming is slow and dependent on biological and climatic factors, it is a successful technique for complete biodegradation. This study will investigate in the field the extent of hydrocarbon degradation. As for Shailubhai's conclusion regarding the slow rate of biodegradation in the field, this can only be determined by conducting studies such as the realized one.

Madsen (1991) stated that determining in situ biodegradation is an essential step in the development and validation of many technologies aimed at alleviating environmental

pollution. However, he acknowledged that it is difficult to prove in situ biodegradation in the field because of the difficulties in conducting mass balances, as well as distinguishing between biotic and abiotic attenuation. He also stated that the documentation of in situ biodegradation is relatively rare and almost always qualitative; laboratory experiments have provided most of the information presently available on different aspects of the biodegradation of organic compounds.

Schlauch and Clark (1992) stated that bench-scale studies to determine if a contaminant is biodegradable might not accurately represent the biodegradation potential and rate of degradation of a contaminant in field situations. This conclusion was the result of both laboratory studies and field studies conducted by Radian Corporation in order to evaluate the optimum conditions for a full-scale bioremediation project to be conducted at a superfund site in Clovis, New Mexico. The results of these studies showed that hydrocarbon degradation rates obtained in the field were much greater than those obtained in the laboratory. The field results yielded approximately 70% to 80% degradation of TPH in contaminated soil, while the laboratory results showed a decrease up to 40% only.

Rates of application and degradation are two important factors that show the effectiveness of the biodegradation process. The waste application rate is the amount of waste that is applied per unit area of land. For optimal use of a landfarm, the highest rate of sludge application that will not adversely affect the rate of biodegradation is desired (Texas Dept. of Water Resources 1976). Martin et al. (1986) stated that the rate of

application is a function of oil concentration in the waste and the land area for waste treatment, assuming a conventional 15-cm depth of incorporation. Arora et al. (1982) reported the results of a laboratory experiment conducted by Neal in 1980 to study the effect of oily waste application rate on microbial populations. He concluded that the bacteria population was greater in columns receiving a low application rate than those receiving a high application rate because of the decreased aeration from excessive hydraulic loading. Arora reported the highest increase in microbial population at an application rate of 1.2 cm/week of oily waste. Bindra and Zestar (1979) reported maximum oil loading on a landfarm as 20% of oil by weight, and stated that higher oil loading would make the soil hydrophobic and might impair oxygen transfer. Brown (1981) concluded that smaller and more frequent applications of oily sludges result in higher biodegradation rates than does infrequent application of larger batches. He also stated that the optimum application rates for wastes from petroleum refineries and from petrochemical plants was from 5% to 10% (wt/wt). Jenson (1975) reported that the highest oxygen uptake rate and the greatest total microbial counts occur at an oily waste concentration of 5%.

Dibble and Bartha (1979a) conducted a laboratory study to determine the effect of the loading rate on oily sludge biodegradation: five different loading rates (0.25, 0.5, 1, 2 & 3 g) of extractable hydrocarbons per 20 g of soil were add to five flasks and incubated for 130 days. Afterward, second loads of the same extractable hydrocarbons were added using the same loading rates as with the first charge, and the flasks kept for an additional 155 days. Based on the calculation of CO_2 evolution, the result showed that the highest

percentage of biodegradation occurred at the lowest application level (0.25 g/20g of soil). However, the authors stated that CO_2 evolution should not be considered alone but that residual hydrocarbon level should also be considered. They concluded that the maximum useful loading rate was one g of hydrocarbon per flask because the best compromise between the high degradation rate and the low residual level was at this loading rate. This recommended loading rate translates into 255 barrels of hydrocarbon per acre. Concawe (1980) recommended a loading rate of oil should not exceed 15 kg/m^2. All of these studies agreed on the importance of having low application rates of oily sludges, however, more work is needed in order to identify the rate of application that will result in the optimal degradation rate.

Several factors affect the rate of degradation: type of sludge, type of soil, microorganisms in the soil, loading rate, and the climate (Shailubhai 1986). Degradation rates are generally expressed as half-lives, or the time required to decrease the original concentration by one-half of the initial level. Loehr (1986) reported that half-lives could be estimated from first-order kinetics, if first-order rate constants are known for waste constituents. The first order reaction used is $dC/dt = -KC$; this indicates that at any time, t, the rate of degradation is proportional to the concentration, C, of the chemical in the soil. Taylor and Viraraghavan (1999) conducted a bench-scale investigation to study the degradation rates of diesel-contaminated soil under different treatment conditions, and concluded that the greatest degradation rate was obtained with the addition of nutrients. They estimated the first order degradation rate constant (K) with the addition of nutrient to be $K=0.19$ $week^{-1}$ and without nutrient to be $K=0.07$ $week^{-1}$. Schlauch and Clark

(1992) concluded that the degradation rate constant (K) for oil and grease was K=0.04 $week^{-1}$. Roberts (1998) listed some biodegradation rates observed in land treatment operations (Table 2.1). When evaluating this table, it is obvious that loading and degradation rates differ from place to place. The range of loading rates is from 11 to 148 g/kg soil/year and the range for degradation rates is from 6 to 165 g/kg soil/year. The question of which rates should be used in arid regions cannot be answered, as there is no single number to be used; rates should be determined for each area alone. For the first time, this study made an attempt to determine, through field experiment, the degradation rate constant (K) of tank bottom oily sludge in arid regions.

Table 2.1 Biodegradation rates reported from full-scale land treatment operations

Waste	Location	Loading Rate g/kg soil/year	Loading Rate lb/ft^3 soil/year	Degradation Rate g/kg soil/year	Degradation Rate lb/ft^3 soil/year
Refinery oily-	Montana	11	0.98	6	0.57
waste	California	148	12.25	114	10.28
	New Jersey	87	07.82	61	05.47
	Illinois	16	01.40	11	00.98
	Louisiana	44	04.00	39	03.52
	Washington	22	01.97	14	01.26
	Texas	29	01.97	22	01.96
	Texas	79	07.16	75	06.73
	Texas	62	05.62	55	04.94
	Oklahoma	67	06.00	53	04.80
	Oklahoma	17	01.54	11	00.98
	Texas	----	----	165	15.00
Heavy oil	Oklahoma	1.2	0.11	0.5	00.05
Sulfite wastes		<150 lb BOD/acre/day		100%	
Vegetable-canning wastes		1300 lb COD/acre/day		99%	

Source: Roberts (1998)

2.4 Parameters Influencing Landfarming Performance

The effectiveness of landfarming processes depends on several important parameters that can be grouped into three categories: sludge characteristics, soil characteristics and condition, and temperature (Arora et al. 1982; Berkowitz et al. 1983; US EPA 1998). The information available in the literature specifies the parameters for each category and provides actual values for each parameter that, according to the authors, will result in an optimal degradation rate for oily sludges. However, after evaluating the literature, two important issues were noted. First, most of the literature provided a range of values for each parameter instead of providing one single number. For example, in the case of temperature, the optimal temperature range was reported to be between 20-35° C (Rast 1997) while Dotson et al. (1972) concluded the optimal range was between 30° and 40° C. Second, recommended values for the same parameters varied significantly. This is particularly evident when noting that Brown and Donnelly (1983) and Sandvik (1986), reported optimal temperatures of 18°C and 30° C respectively. According to Shailubhai (1986), important parameters such as the effect of tilling, soil texture and fluctuation in temperature during a 24-hour cycle have not been studied.

2.4.1 Sludge Characteristics

Oily sludge is predominantly a water and oil emulsion with napthalenic and other waxes present, as well as some iron oxide scale (Arabian American Oil Company 1984). In the oil industry, oily sludge is generated from several sources. Concawe (1980) lists different types of sludges produced in oil refineries (Table 2.2). Not all of the sludges listed in this table are suitable for landfarming. Sludge that contains toxic substances such as organic

lead or non-degradable components such as plastics, rags and domestic refuse are less suitable for landfarming (Concawe 1980).

Table 2.2 Types of sludge generated in oil refineries

Type of Sludge	Typical Quantity (tons/ year per refinery)	Composition (% weight)		
		Oil	Water	Solids
TANK BOTTOMS				
Small refineries	100–400	30-60	70–40	Solid
Large refineries	500-3000	40-60	60-40	sediments
DESALTER BOTTOMS				
1(a)	60	5	85	10
2(a)	70	30–40	30–40	20–40
GRAVITY (API) SEPARATOR				
BOTTOMS Group 1 refineries (b)	100-2500	10-20	50-80	10-30
Group 2 refineries (b)	2500-20000	10–40	60-90	5-20
FLOCCULATION D.A.F.SLUDGE				
Group 1 refineries (b)	500-2500	40	55	5
Group 2 refineries (b)	2500-20000	1-10	80-98	1-10
FINAL TREATMENT SLUDGE				
Cake from filtration	3000	10	70	20
Centrifuged sludge	2000	8-10	80-90	10-12
Biological sludge	3000	0.1-0.5	80-90	10-20
OPERATING SLOPS AND OIL				
SPILLS	50-100	30-70	70-30	--
Liquid slops	100-200	100	--	--
Grease, wax and paraffin slops	30-70	30–40	--	60-70
Liquid spills	50-300	100	--	--
Asphalt spills				
OPERATING RESIDUE				
CHEMICALS				
Spent caustic	1000	Traces	90	10
Lime	5000	--	--	100
OTHERS				
Cooling tower waste	30-50	1-2	95	3-5
Clay from lube oil treatment	300-1000	30-60	1-5	70–40
SLUDGE CONTAINING LEAD*				
TEL/TML Sludges	10-250	ppm.	1-10	90+lead
MISCELLANEOUS WASTES				
Gravel, earth, sand, silt	500-1000	0-2	0-10	88-100
Oily solids	1-200	10	--	90
General wastes	1-300	--	--	100
Cracking fines	100-200	sometimes	--	100

Source: Concawe (1980)

Remarks

(a) Depending upon the process used

(b) Group 1 refineries are hydro skimming refineries, usually with capacities up to 5 million tons per year Group 2 refineries are more complex, typically with cracking units and often larger than Group 1 refineries

* Must be treated separately

The composition and the loading rate of sludge are the most important sludge factors that affect the degradation process. Controlling these sludge factors will lead to maximizing the rate of degradation (Bossert et al. 1984; Dibble and Bartha 1979a; Concawe 1980; Beak Consultants 1981; American Petroleum Institute 1983).

The chemical structure of oily sludge is an important determinant of its susceptibility to the biodegradation process. The rate at which a compound is biologically broken down might increase or decrease depending on the presence of functional groups in the hydrocarbon chain or the aromatic ring (Kretschek and Krupka 1984). Bindra and Zestra (1979) added that straight chain paraffin is the easier group of hydrocarbons to degrade and that the rate of decomposition decreased drastically by branching of the paraffin chain.

2.4.2 Soil and Climatic Conditions

Soil is the media where all of the degradation processes take place. It provides a natural environment for the biodegradation of waste materials through complex physical, chemical and microbiological processes. The presence of suitable microorganisms, the availability of water, nutrients and oxygen, and the soil texture and pH are the most important soil factors that affect the degradation processes. Controlling these soil factors will lead to maximizing the rate of degradation (Concawe 1980; Arora et al. 1982; American Petroleum Institute 1983; Riser-Roberts 1998; Potter and Simmons 1998).

Most of the literature provides a thorough description of the soil factors and their effect on the degradation rates. However, it appears that the figures presented in most of the literature were based on operational reports (in particular Concawe), and on a few laboratory studies that were conducted during the 1970s and 1980s. Concawe, which many literature used as a reference, stated that loamy soil is the ideal soil; however, clayey or sandy soils are also suitable. According to the Concawe, the sand would allow better oxygen diffusion and enhance microbial activity, but at the same time might allow leaching of the oil as well as precipitation. Furthermore, clay would provide better containment of the sludge, but its low permeability can inhibit the infiltration of water and oil and will result in poor aeration and thus result in anaerobic conditions. Concawe also reported that the decomposition rate of 0.25 kg oil/m^3/day has been measured without the addition of fertilizers and that this rate may rise to 0.5 kg/m^3/day if fertilizers are added. The report recommended a carbon to nitrogen to phosphorus ratio of 100:10:1 with a pH range from 6.5 to.7.5.

Kretschek and Krupka (1984) have presented a thorough description of all the soil factors that affect the degradation of oily wastes. They concluded that aerobic degradation is the most desirable microbial process for breaking down petroleum hydrocarbon contaminants because it proceeds at a more rapid rate and does not produce the noxious by-products associated with anaerobic decomposition (e.g., methane, hydrogen sulfide). They also stated that microbes that have been shown to metabolically alter waste materials include species of actinomycetes, fungi, bacteria and photosynthetic microorganisms such as

algae, cyanobacteria and photosynthetic bacteria. Many of these commonly occurring microorganisms are found in the local soil environment.

Rast (1997) noted that for petroleum hydrocarbons approximately 3.5 pounds of oxygen are required per pound of hydrocarbon. Since tilling increases the diffusion of oxygen from atmosphere into the soil due to higher soil porosity and incorporation of air into soil voids, the soil at landfarms should be tilled regularly. Near-neutral pH values are most favorable to microbial functioning in general, but, Rast suggested a range of pH 7.0 to pH 8.5 is acceptable: the optimal growth of microbial populations responsible for the biodegradation of petroleum products occurs between 20 °C and 35 °C.

Brown and Donnelly (1989) conducted a series of laboratory tests to determine the influence of soil texture, temperature and moisture content on the optimum conditions for the degradation of refinery sludges. Various types of soil and moisture contents were utilized under different temperature ranges Their results showed that maximum degradation would occur in sandy clay soil at a moisture content of 18% and a soil temperature of 30°C. The degradation rates were measured by CO_2 evolution and residual hydrocarbon extraction. Their results showed that the half-life of refinery sludge as determined by CO_2 evolution was 130 days, and by residual hydrocarbon extraction as 143 days. However, they concluded that the degradation rates in the field might be different because of temperature fluctuations, variable soil moisture, and acclimatization of the microorganisms. More fieldwork is needed to verify the findings of this study. Dibble and Bartha (1979a) conducted a laboratory study to optimize the environmental

parameters (moisture content, pH, nutrients and temperature) of oily sludge biodegradation. Their results showed that the optimal degradation rate was achieved at a soil water holding capacity of 30-90%, a pH of 7.5 to 7.8 and a carbon to nitrogen to phosphorus (C:N:P) ratio of 100:10:1, at a temperature at or above 20°C. The authors concluded that laboratory results can be helpful but will not represent actual field conditions; this is due to limitations in parameters that could not be tested in the laboratory such as the fluctuating temperature in the field, aeration, and to some extent soil texture. They also pointed out that their findings would need validation and possible adjustment in the field.

Sandvik et al. (1986) reported the results of both laboratory and field experiments where they studied the degradation rate of oily sludge in landfarms under Norwegian conditions. In these experiments, several cells were constructed and tested against two types of soils, temperature, and the addition of fertilizers. The results showed that while the degradation process under South Norwegian conditions occured, the oil content was reduced by 45% after nine months and 83% after 32 months. The optimum temperature was determined to be 18°C. The addition of fertilizers reduced the oil content by 45% after nine months, compared with a reduction of 4% in the cell that did not receive any fertilizers. The ratio of the added fertilizers was 25:3:6 as nitrogen-phosphorous-potassium, respectively, and the added amount of N was 600 kg per hectare per year. The time to achieve this degradation rate (32 months for 83% degradation) seems to be long. Block et al. (1993) reported that bioremediation typically takes between two months to two years to complete. The longer time needed, indicated by Block's study, is probably due to the cold

temperature. It is important to mention that most of the studies reported above were conducted in the laboratory, with a few being conducted in the field.

Temperature exerts a major control on the metabolic activity of microorganisms because the entire microbiological organic breakdown occurs through the activity of enzymes. As the temperature increases, the rate of metabolic activity increases due to the presence of more energy in the system. Kretschek and Krupka (1984) stated that microbial activities increase until an upper limit of approximately 45 °C is reached and that beyond this temperature, microbiological activities decrease and eventually cease. They also stated that some thermophillic organisms have been found to thrive at temperatures between 55° and 60 °C. Shailubhai (1986) discussed the importance of these factors and stated that the biodegradation of oily sludge in soil is carried out mainly by aerobic microorganisms present in the top 6-8 inches and that anaerobic microorganisms will degrade oily sludge in anaerobic conditions as long as nitrates, nitrites and sulfates are present. The nitrites, nitrates, and sulfates will serve as an alternative to oxygen (electron acceptor) for the oxidation reaction where electrons are transferred from the oily sludge hydrocarbons to the terminal electron acceptors. As for the nutrients, Shailubhai indicated that the addition of fertilizers would lead to doubling the amount of degraded oily wastes (although this statement needs to be verified). Arora et al. (1982), in their discussion on biodegradation, stated that more than 100 species of bacteria, fungi, actinomycetes and yeast are known to attack one or more types of petroleum hydrocarbons. They also stated that the distribution of microorganisms in the soil varies and that the upper soil zone contains by far the largest microbial population and they concluded that the upper soil zone is the

most active zone. Table 2.3 was used by Arora et al. (1982) to show the distribution of these microorganisms in the soil zones. This table shows that the population of both aerobic and anaerobic bacteria is more at the upper soil surface than it is through out the lower zones.

Table 2.3 Distribution of microorganisms in a soil profile

(Organisms per gram of cell)					
Depth (cm)	**Aerobic Bacteria**	**Anaerobic Bacteria**	**Actinomycetes**	**Fungi**	**Algae**
3-8	7,800,000	1,950,000	2,080,000	119,000	25,000
20-25	1,800,000	379,000	245,000	50,000	5,000
35-40	472,000	98,000	49,000	14,000	500
65-75	10,000	1,000	5,000	6,000	100
135-145	1,000	400	-	3,000	-

Source: Arora et al. 1982

Viraraghavan and Robbins (1995) reported the result of a study conducted by the University of Regina to determine if the Regina area in Saskatchewan, Canada is suitable for land treatment of refinery wastes. The results indicated that land treatment is a viable disposal option and that degradation will occur in cold regions. This study reported that the ideal soils are loam, silt loam or sandy loam with a pH between 6.5 and 8.5 and that most soil microorganisms are active at a temperature between 20 °C and 35 °C. However, the types of microorganisms in Regina were most active between 35 °C and 45 °C. The study also showed that the level of bacteria in Regina was low between November and March and that the optimum number is reached in July. The levels of bacteria in the summer were approximately 75% of those in the Southern USA. The addition of fertilizers reduced the degradation time by 50%. The study concluded that excessively

permeable soils such as sand and gravel are unacceptable for landfarming and that the ideal soils for land treatment processes are loam, silt loam or sandy clay loam.

Salanitro (2001), in his review of literature on the biodegradation of representative hydrocarbons, stated that there is a wide variation in the use of nutrients as soil amendments to enhance biodegradation. He quoted several studies where the results showed that the addition of nutrients had no significant effect on the rate of biodegradation. He also discussed the results of other experiments where hydrocarbon decline was significantly enhanced with the addition of nutrients.

Huesemann (1994) stated that a wide range of C:N and C:P ratios have been reported in the literature. He also stated that while Frankenberger recommended a C:N:P ratio of 100:10:1 (Frankenberger 1991), Dibble and Bartha (1979a) found optimal oily sludge biodegradation with C:N and C:P of 60:1 and 800:1 respectively.

2.5 Bioreactor Technology

A review of the literature showed that limited research has been conducted using controlled and engineered biotreatment systems either as a replacement for or in conjunction with landfarms (Lapinskas 1989; Brown et al. 1990; McNicoll et al. 1995; Oliver et al. 1998; Kinney e al. 1999). These studies referred to controlled biotreatment systems such as bioreactors, biopiles, engineered soil banks and bed land treatment.

Shailubhai (1986) concluded that even though oily sludge biodegradation in soil is successful, it is a slow process. In his recommendation, Shailubhai also mentioned that

oily sludge biodegradation in a temperature controlled aerobic system can be enhanced by inoculation of highly efficient oil degradation microorganisms along with some mineral nutrients. In order to determine if his recommendation is sound, a field study need to be conducted so that the results obtained from landfarm cells and those obtained from closed aerobic cells can be compared.

McNicoll et al. (1995) used an above ground bioreactor system to treat an estimated 3600 tons of petroleum-contaminated soil. The objectives of this study were (1) to quantify how much of the degradation is attributed to leaching, volatilization and biodegradation, and (2) to assess the effect of temperature and nutrients on the rate of biodegradation. Four cells were constructed, of which two served as control cells (one for temperature and one for nutrients). McNicoll reported that 97% of the total petroleum hydrocarbons were reduced in all four cells during a period of six months. The reduction attributed to the degradation process was estimated to be 99% while the reduction resulting from volatilization was estimated to be 0.5%. The leaching effect was negligible. These figures were obtained from mass balance calculations. The authors also reported that there were no significant differences between the nutrient control cell and the remaining cells. Their attempt to generate a difference between the temperature-controlled cell and the other cells was not successful due to a relatively higher exchange rate. However, they stated that the bacteria count had a significantly positive correlation with soil temperature for temperatures up to 10 °C and that between 10 °C and 26 °C, there was no significant effect. These results need to be compared with other studies. Although the degradation rate was much faster, the question about the effect of bacteria and nutrients is not clear.

To state that 99% of the degradation was attributed to the biodegradation process is also questionable. No other studies were found in the literature that could be compared with this one. Finally, this work was conducted in a cold climate and thus these results could be much different if such a test was conducted in an arid region.

Brown and Cartwright (1990) suggested combining the landfarming and bioreactor processes. They stated that the sludge should be treated at a landfarm as a first stage to achieving a gross reduction in the hydrocarbon content from a percentage level to the thousands ppm level and that the treated sludge should then be placed inside a bioreactor where a final reduction would be achieved. This recommendation was based on theory. None of the literature reported any studies similar to what Brown recommended. This study has attempted for the first time to combine both technologies together.

Chapter 3

Experimental Approach

3.1 Introduction

The main focus of this study was to determine the degradation rate of oily sludge in a landfarm under the field conditions of an arid region. The degradation rates and parameters affecting degradation in the past were mainly studied in the laboratory with very limited research conducted in the field. Most of the studies in the laboratory were conducted on either hydrocarbon products or sludge generated from API separators.

In this study, a full-scale field experiment that is most representative of field conditions under arid climate was conducted. Various planned activities within this study were: site selection, experimental layout, design, construction, and operation of the cells, sludge application, sampling procedures and laboratory work. These activities are discussed in the following subsections.

3.2 Site Selection

The three factors considered when the test site was selected were: geographical location, site hydrology, and climatic conditions.

3.2.1 Geographical Location

To assess the effectiveness of the landfarming method under arid climatic conditions, the location of the field-scale experiment was selected inside the Juaymah Oily Waste Landfarm, which is located in the Eastern Province of Saudi Arabia. This landfarm was constructed in 1994 and is located 20 km northwest of the Ras Tanura Refinery (the largest refinery in Saudi Arabia with a refining capacity of more than 350,000 barrels/day) and 2 km southwest of the Arabian Gulf (Figure 3.1).

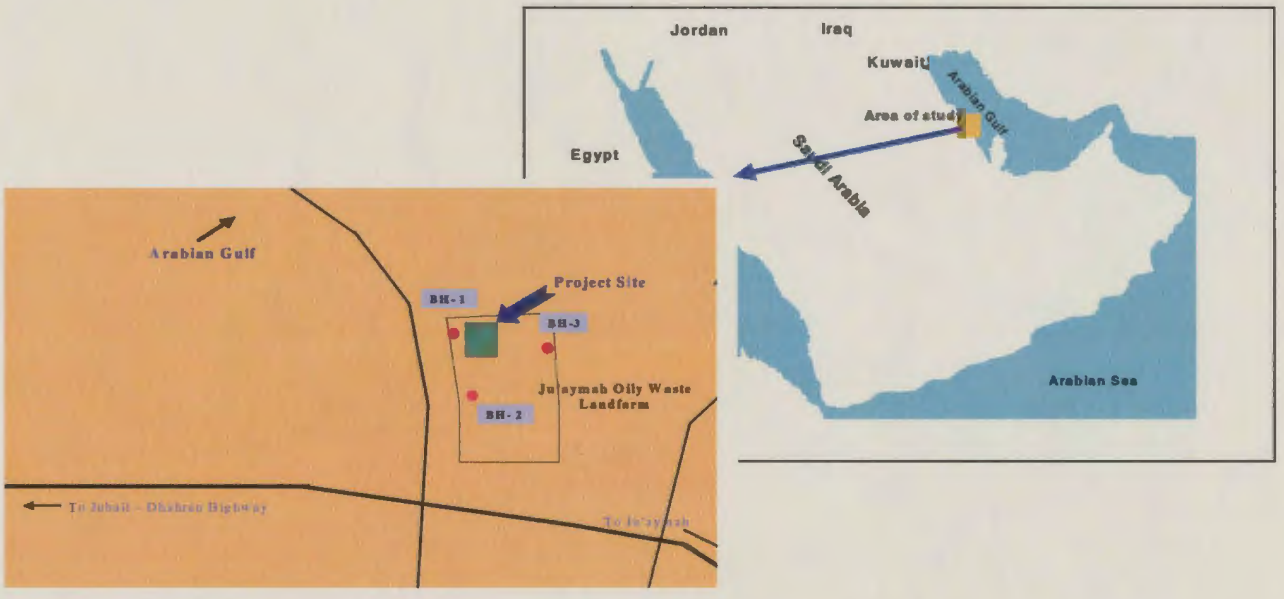

Figure 3.1 Map showing the geographical location of test site

3.2.2 Site Hydrogeology

The test site is a low-profile sand dune field over a widespread marine *sabkhah*. Sediment deposits in the sabkhah include sand and clay. The top 1.2 m of the surface is mainly sand. Localized and shallow groundwater has some fresh or slightly brackish characteristics, as it is predominantly generated from rainfall that has been trapped (perched) in the shallow dune sediments. The depth of the groundwater at the site is approximately 6.6 m. This depth meets the requirement set by Concawe (1980) that the water table in the selected landfarm site should be at least 1-2 meters below ground level. Morgan et al. (1989) also stated that when choosing a landfarm site, the water table should be below a depth of 1.5 meters. A depth of 1-2 meters represents the minimum requirement for minimizing the risk of groundwater contamination due to the leaching of hydrocarbons. Three monitoring wells (BH-1, BH-2 and BH-3) exist inside the Juaymah landfarm, one up-gradient and two down-gradient (Figures 3.1). These wells are used to directly monitor potential environmental impacts from site operations. The total dissolved solids in the water ranges from 3,500 mg/L to 6,000 mg/L, making the shallow water suitable for livestock, but essentially unsuitable for human consumption. An analysis of the water obtained from these wells since 1994 did not show any contamination due to the operation of the landfarm. This study focused on biodegradation and evaporation processes. The effect of leaching was not included due to the following reasons:

- The water table is more than 6 meters in depth.
- Rainfall in the area is less than 3.4"/year.

- Samples colleted from the groundwater monitoring wells at the site did not show any indication of groundwater contamination

3.2.3 Climatic Conditions

Meteorological data collected near the site between 1964 and 1984 showed that the average annual rainfall in this area is approximately 3.4" (85.6 mm) and the average annual evaporation is approximately 86" (2190 mm), which clearly indicates that this area can be classified as an arid region. A meteorological station located near the test site was used to obtain rainfall and air temperature data during the study period.

3.3 Experimental Layout

The objectives of this study include studying the kinetics of oily sludge degradation in landfarm and bioreactor cells under natural and enhanced conditions (i.e., water, nutrients and tilling). As per the factorial experiment design method, to study the individual and combined effect of these conditions, a total of eight landfarm cells and eight bioreactor cells are required (Brethouex and Brown 1994). To study the effect of increasing oily waste loading and combining landfarm and bioreactor methods, three more cells are needed. This leads to a total of 19 cells; however, studying 19 cells was not possible due to the following reasons:

- Operating 19 experimental cells was cost prohibitive.
- The analytical support for 19 cells was not technically feasible.

As a result, it was decided to reduce the number of cells from 19 to 11. Because landfarming was the main subject of this research, seven cells were devoted to landfarm study and four cells to bioreactor study. Since tilling is the most applicable enhancement method in landfarm applications, four cells were assigned to study the individual and all possible combinations of tilling with other enhancements. The remaining three cells were assigned to study the effect of (1) natural attenuation; (2) loading rate; and (3) combining landfarming with bioreactors.

Two of the four bioreactor cells were devoted to study the effects of all enhancements together, while the other two were devoted to natural attenuation and combination with the landfarm cell. Table 3.1 depicts the assignment of the 11 cells.

Table 3.1 Assignment of cells designation

Plot	Tilling	Watering	Fertilizers	Double Load
LF1 (natural attenuation)				
LF2	+			
LF3	+	+		
LF4	+		+	
LF5	+	+	+	
LF6	+	+	+	
LF8	+	+	+	+
BR1	+	+	+	
BR2	+	+	+	
BR3	+	+	+	
BR4 (natural attenuation)				

The functions and the experimental work carried out in each of the landfarm and bioreactor cells are described below.

3.3.1 Landfarm Cells

LF1 (No Action): This cell was selected as the control landfarm cell. The sludge was applied and periodical monitoring was conducted without any action to enhance the degradation of the sludge. This cell was used to evaluate the natural attenuation of the sludge.

LF2 (Tilling): In this cell, tilling was applied once a week to a depth of 8 inches to provide aeration to the microorganisms inside the incorporation zone. This cell was used to investigate the effect of tilling on the degradation process.

LF3 (Tilling + Water): This cell is similar to LF2, except that water was added to the incorporation zone. This cell was used to investigate the effect of tilling and moisture content on the degradation process.

LF4 (Tilling + Nutrient): Besides weekly tilling, nutrients were also added in this cell. The frequency and application rate of nutrients was based on those reported by Concawe (1980). This cell was used to investigate the effect of tilling and nutrients without the addition of water on the degradation process.

LF5 (Tilling + Nutrient + Water): In this cell, nutrients were added with the sludge. Aeration and moisture content were also adjusted periodically. This cell was used to investigate the effect of nutrients, tilling and water on the degradation process.

LF6 (Tilling + Nutrient + Water): This cell is similar to LF5. The intention here was to investigate the effect of combining both landfarming and bioreactor methods with respect to achieving the highest rate of degradation and a condition where the percentage of oil content would be reduced considerably. The plan was to remove the sludge from this cell if the oil content reduced by 75-80%, and to place it inside BR1. The work in this cell was terminated in February 2001 when it was clear that the decrease in oil content was not that significant.

LF8 (Tilling + Nutrient + Water): Work in this cell is similar to LF5, except the oil content was doubled. The loading rate was 300 g of sludge/kg of soil. The goal here was to investigate the effect of hydrocarbon loading on the rate of degradation.

3.3.2 Bioreactor Cells

The main objectives of constructing the reactor system was (1) to quantify the VOCs generated from the degradation of oily sludge; (2) to compare the performance of landfarms with bioreactors; and (3) to integrate landfarming and bioreactor systems to optimize the degradation rate. A brief description of these cells is as follows:

BR1 (Air + Nutrient + Water): The purpose of this cell was to apply the sludge mixture from LF6 once the oil content was reduced by 75-85% with the intention to investigate the effect of combining landfarming and bioreactors to achieve the highest rate of

degradation. Since the reduction in the oil content was not significant in LF6, this cell was never used.

BR2 (Air + Nutrient + Water): In this closed cell, nutrients were added with the sludge. Air and water were added on a weekly basis. This cell was used to investigate (1) the effect of oxygen and water on the degradation process in a closed reactor (top covered with clay), and (2) to collect generated VOCs to assess the health risk to onsite workers (Figure 3.2).

Figure 3.2 Collection of VOC from bioreactor cell (BR2)

BR3 (Air + Nutrient + Water): This cell is similar to BR2, except that it was not covered with a liner. The intentions here were i) to compare the performance of this cell with BR2, and ii) to investigate the effect of adding oxygen and water mechanically on the degradation process and to compare the results with LF5 (where air and water are added manually).

BR4 (No Action): In this closed cell, the sludge was applied and periodical monitoring was conducted without any action to enhance the degradation of the sludge. This cell was used to investigate the natural attenuation process of the sludge in the bioreactor without any action.

3.4 Design, Construction, and Operation of Cells

3.4.1 Design of Cells

The design of the landfarm cells was based on the design specification listed by Concawe (1980) and the American Petroleum Institute (1983). Figure 3.3 shows the detailed design of a landfarm cell.

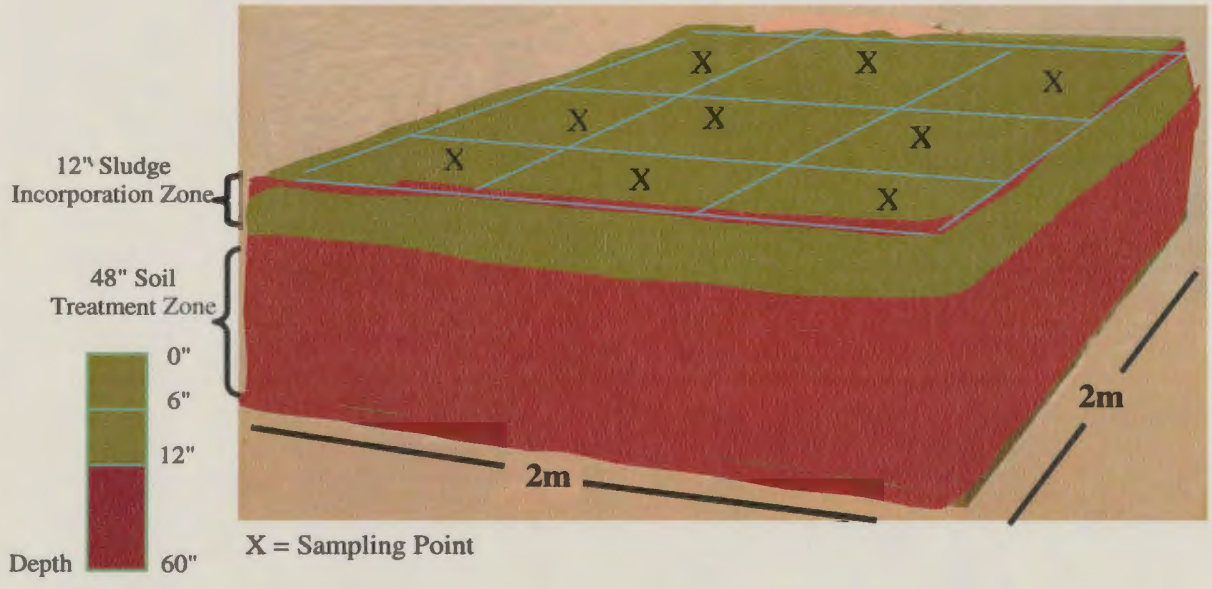

Figure 3.3 Landfarm cell showing incorporation and treatment zones with sampling points

The design of the bioreactor cells was based on the design specified by Brown and Cartwright (1990) and McNicoll and Baweja (1995). Figure 3.4 shows the detailed design of a bioreactor cell.

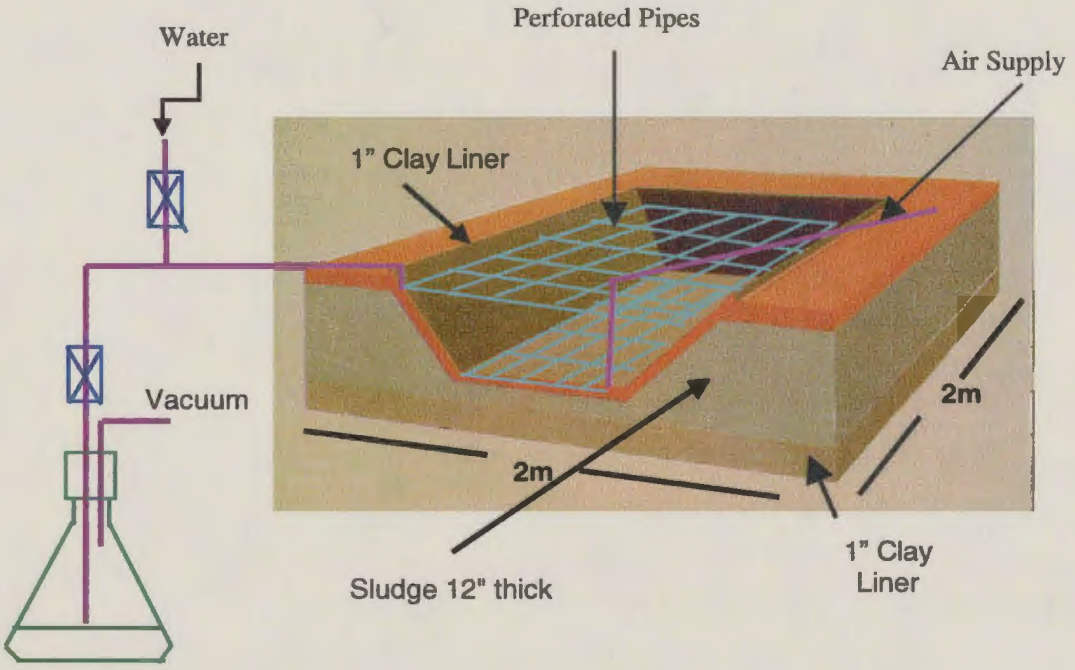

Figure 3.4 Sketch of a bioreactor cell showing perforated pipes, liners, air, and water supply lines and vacuum connection for collecting VOCs

The layout of the landfarm and bioreactor cells and the types of applications and experiments that were performed in each cell are shown in Figure 3.5. The seven landfarm cells are referred to as LF1 through LF6 and LF8, and the four bioreactor cells as BR1 through BR4.

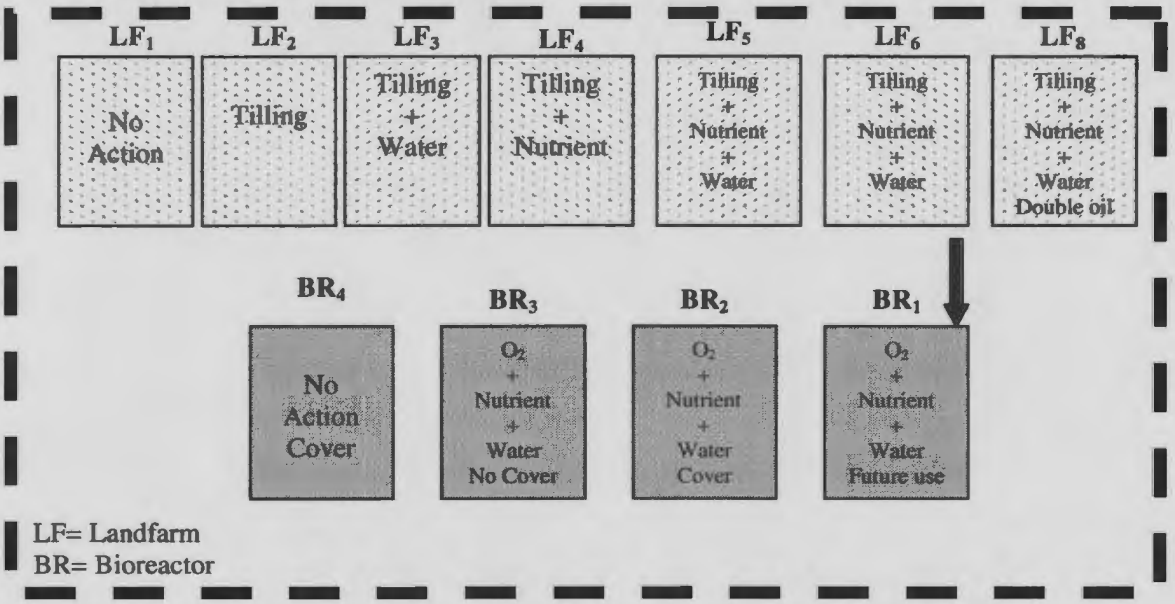

Figure 3.5 Plan of test site showing all cells and the applied treatment at each cell

3.4.2 Construction of Cells

An area of land 21 x 15 meters at the northeast corner of the Juaymah landfarm was used to conduct the fieldwork. The land contained clean sand that had never been used for any disposal activities. The area was divided into two lots: the first contained seven cells that were designed, constructed and operated as landfarms, while the second lot contained four cells designed, constructed and operated as bioreactors. The size of each cell was 2 x 2 meters. The construction of these cells started on August 23, 2000 and was completed on September 13, 2000 (Figure 3.6).

Figure 3.6 Construction activities at the site

The landfarm cells were not lined, while the bioreactor cells were lined with a one-inch clay liner. Each bioreactor cell contained two sets of perforated pipes (Figure 3.7). The first set, located at the bottom of the cell, was used to inject air with a compressor to provide an essential source of oxygen for the proliferation of the hydrocarbon degrading microbes. The top set, with a dual function, was used to inject water and also to collect VOCs and other gaseous byproducts generated as a result of sludge degradation. Both sets of pipes were designed to introduce water and air uniformly.

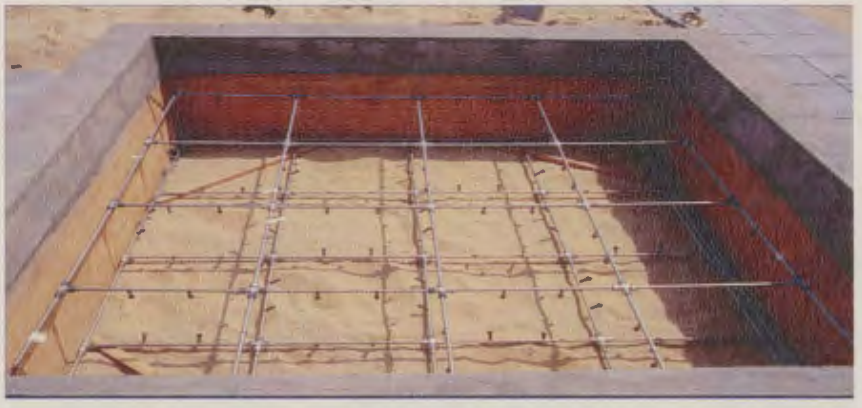

Figure 3.7 Two sets of perforated pipes inside the bioreactor cells

3.4.3 Operation of Cells

The sludge used in this study was obtained fresh from the bottom of a one-million-barrel-size tank that contained Arab Medium crude. It was obtained during a scheduled maintenance, which was conducted once every 7 to 10 years. Arab Medium crude represents one of the largest categories of crude generated in Saudi Arabia.

Following the removal of the crude from the tank, air was blown inside the tank for a period of 2 to 3 weeks until the VOC levels were reduced to an acceptable level for personnel to safely enter the tank to carry out the sludge removal operation. This was followed by the use of jetted water to liquefy the sludge and to push it towards one of the maintenance hatches at the side of the tank. The liquefied sludge was then pumped out and collected inside 55-gallon drums. A total of 19 sludge filled drums were brought to the site on September 21, 2000 to be used for this study (Figure 3.8).

Figure 3.8 Loading the 19 drums at the test site

The sludge was applied directly from the drums to the landfarm cells to simulate the actual field application, and was left for several hours on the surface to allow for

penetration before it was thoroughly mixed with the sand underneath (Figure 3.9). Attempts were made to mix the sludge with the sand up to a depth of 12 inches using shovels; however this was difficult to achieve in the field. It was estimated that the mixing was thorough to a maximum depth of 10 inches (Figure 3.10).

Figure 3.9 Application of the sludge into the landfarm cells

Figure 3.10 Mixing sludge with sand inside the landfarm cells

The sand was manually removed from each bioreactor cell; the sludge was added to the sand and mixed thoroughly (Figure 3.11).

Figure 3.11 Mixing sludge and sand outside the bioreactor cells

The mixed sand and sludge were placed inside the bioreactor cells to a depth of 12 inches (Figure 3.12). The loading rate used in this research was 150 g of sludge/kg of soil, which was based on the highest loading rate reported in the literature (Roberts 1998). The selection of this high rate was based on the hot and arid climatic conditions in Saudi Arabia, which was expected to result in higher degradation due to speed up of bacterial metabolism (following Arrhenius law) and more volatilization. The weight ratio of sludge to sand in both the landfarm and bioreactor cells was approximately 1:7. Each cell had 2,340 kilogram of sand and 350 kilogram of sludge, with the exception of cell LF8, which had 700 kilogram of sludge and 2,340 kilogram of sand. The brand name fertilizer Phostrogen was used in this study. The N:P:K ratio of Phostrogen was 84:5.2:5.5. One kilogram of Phostrogen was added to each of the following cells: LF4, LF5, LF6, LF8,

BR2 and BR3. The C:N ratio used in this study was 87:1. This is in line with the recommended ratio (Huesemann, 1994; Salanitro, 2001).

Figure 3.12 Placing the mixed sludge and sand inside the bioreactor cells

The fertilizer (in powder form) was manually added to the sludge and sand as they were mixed together without being dissolved in water. Following the placing of the sand and sludge mixture inside the bioreactor cells, an apparent one-inch-thick layer of clay was placed on top of BR2 and BR4. This layer was intended to act as an impermeable layer to minimize the loss of VOCs and to allow for the collection of VOCs (Figure 3.4) for risk assessment.

For the period between September 26 and October 24, 2000, the sludge inside the landfarm cells was manually mixed using shovels once every two weeks up to a depth of 10 inches to maintain a homogeneous mixture. When cultivation started on November 7, 2000, it was only possible to cultivate to a depth of approximately eight inches using the

hand-held tilling rake. Between October 4, 2000 and March 3, 2001, tilling was applied and potable water and air were added to the landfarm and bioreactor cells once every two weeks. From March 3, 2001 until September 4, 2001, tilling, water and air were added once every week. The main reason for increasing the operating frequency was to keep the moisture content above 6% by weight; however, it was noted that when the landfarm cells were watered, the water evaporated almost immediately. The quantity of water added to each cell was approximately 55 liters each time. The airflow rate to each bioreactor cell was 166 liters/minute. A total of 664 liters of air was injected into each cell at each treatment cycle.

3.5 Sampling Procedures

A sampling protocol was developed to coordinate all of the sampling activities under this research in accordance with EPA methods (Keith 1993). The sampling activities were divided into background monitoring at the initial stage and periodical monitoring on a monthly basis. The background monitoring provided baseline data on soil and sludge. The periodical monitoring was conducted on a monthly basis in order to assess the degradation process in the soil zones. For the landfarm cells, samples were collected from the surface to a depth of six inches using a hand-operated auger. In the bioreactor cells, samples were collected from two zones: from the surface to a depth of six inches, and from 6-12 inches depth (Figure 3.13). Two hand-operated augers were simultaneously used for this purpose to collect samples from the two depths. Samples obtained from each cell were collected in glass bottles and stored in a cooler before being transferred to the

laboratory. Following the sampling from each cell, the augers were decontaminated using inorganic detergents and rinsed with distilled water. In order to assure that the collected samples from the landfarm and bioreactor cells were representative, composite samples were prepared by mixing samples from three different locations from each cell as indicated by 'X' in Figure 3.3. The sampling program commenced on September 26, 2000 and was completed on September 4, 2001.

Figure 3.13 Sample collections from BR2 using hand augers

3.6 Laboratory Work and Analytical Methods

This study required extensive laboratory support to perform the required chemical, physical and biological analyses. The Saudi Aramco laboratories in Dhahran, Saudi Arabia, which performed all the analyses are equipped with advanced analytical instrumentations with well-documented quality assurance and quality control protocols.

Based on a comprehensive literature review and the objectives of this study, a detailed list of parameters to be analyzed was prepared: microbiological parameters, total hydrocarbon, oil and grease, metals, and nutrients (Raymond et al. 1976; Dibble and Bartha 1979a; Huddleston 1979; Concawe 1980). The parameters, equipment used, and methods employed are listed in Table 3.2. Details of the analytical methods are listed in Appendix A.

Table 3.2 Analytical protocol

Parameter	Method	Equipment	Background Sludge	Background Soil	Ongoing Monitoring
Oil & Grease	EPA 9071A (Gravimetric)	Soxhlet/Turbo Vap Concentrator	✔	✔	✔
Total Hydrocarbon	Proprietary Pyrolytic	Rock-Eval 6			✔
BTEX	EPA TO-14	GC-MS			✔
TKN	ASTM D3590-89	Kjeldhal flask	✔	✔	✔
SARA*	SALAM 340-02	HPLC	✔		
N-alkanes	SALAM 340-01	GC-FID	✔		✔
Benzene	EPA 8260	GC-MS	✔		
Micro-organisms	ASTM D933-58	Vials, Incubator, Ultrasonic Bath		✔	✔
Metals**	EPA 6020A	ICP-MS	✔	✔	✔
Nutrients***	EPA 6020A	FIA/ICP-MS	✔	✔	✔
Moisture content %	ASTM D2216-98	Oven & Balance	✔	✔	✔
PH	EPA9045	pH Meter	✔	✔	✔
Soil Texture	ASTM C136-01	Balance / Sieves / Oven		✔	

* SARA: Saturated hydrocarbons, Aromatics hydrocarbons, Resins, and Aspheltene fraction
** Metals: As, Ba, Cd, Cr, Cu, Pb, Mn, Hg, Se, Ag, V and Zn
*** Nutrients: N, P, Na, K, Ca and Mg

Chapter 4

Analytical Results and Discussion

4.1 Introduction

The experimental approach, including site selection, construction activities, experimental design, sampling and laboratory work, was discussed in Chapter 3. In this chapter, the data obtained from the study are analyzed and the performance of the individual cells is evaluated. The analytical results (decrease in O&G concentration) obtained using the Open System Pyrolysis method, which was used for the first time in an oily sludge degradation study, are also evaluated and compared with the results obtained from a typical O&G analytical method.

4.2 Baseline Analysis

The baseline analysis was conducted, as part of the sampling protocol, on soil samples obtained from the surface of the test site prior to any experimental work and on fresh sludge samples obtained from the tank. These analyses were conducted in order to provide the necessary background information for assessing the suitability of the site and the composition of the sludge prior to the beginning of the study.

4.2.1 Soil

Prior to the beginning of any activities in the selected site, soil samples were collected from two locations and analyzed for physical, chemical and microbiological parameters in order to identify the type, composition and characteristics of the soil, and to identify pollutants, if present, at the site.

The grain size distribution of the soil was determined by mechanical sieve analysis and the results were plotted on a semilogarithmic scale (Figure 4.1). The shape of the curve indicated that the grain size is uniform graded. The soil classification, based on grain-size characterization reported by Terzaghi and Peck (1967), showed that the soil is mainly sand.

An experiment, conducted to determine the water-holding capacity of the soil (Appendix B lists the details of this experiment), showed a capacity of 16.5%. Huesemann (1994) stated that the optimal soil moisture range for microbial biodegradation activity is between 50 and 80% of the field capacity moisture content. Dibble and Bartha (1979a) noted that oily sludge biodegradation was optimal at 30-90% of the soil water-holding capacity. This means that the required moisture content to support biological activities in this soil should be between 5.0% and 14.8%.

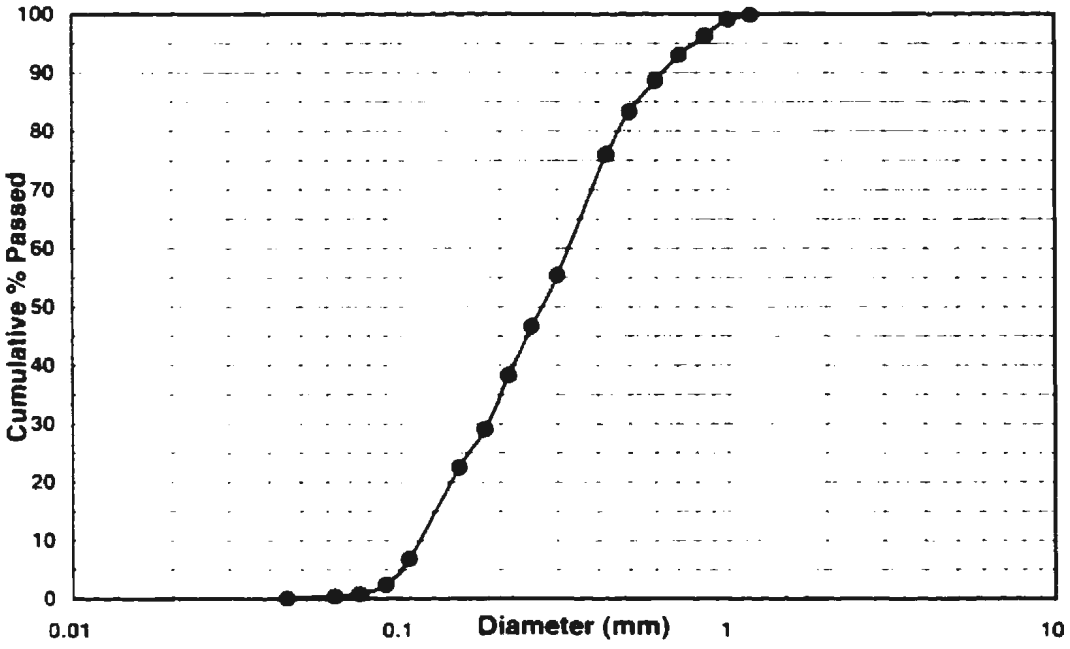

Figure 4.1 Semilogarithmic plot of the sieve analysis for the sand

Table 4.1 lists the average analytical results for the chemical and microbiological parameters of two background soil samples collected from two points within the vicinity of the research site. The analysis showed that the soil did not contain any Oil and Grease (O&G) or benzene. As expected, the soil moisture content was low (0.6%); however, the soil pH was unexpectedly high (9.6). A microscopic analysis was conducted on the sand to determine the cause of this high pH. This high pH was attributed to the presence of calcium carbonate (lime) on the surface of the sand. The General Aerobic Bacteria (GAB) count was 9.3E+03, which is in the low range. This was expected because of the low moisture content in the soil and the absence of any organic material. The nitrogen, measured as TKN, was also low (<100ppm). Heavy metals were low, but calcium and magnesium were high (Table 4.1).

Table 4.1 Background analysis for sludge and soil

Parameters	Background sludge	Background soil
Moisture content %	48%	0.6%
Oil & Grease (mg/kg)	252945	nd
Benzene (mg/kg)	93	nd
General aerobic bacteria (GAB/g)	na	9.3E+03
Metals: (mg/kg)		
Arsenic	6	<1
Barium	123	26
Cadmium	5	<1
Calcium	42780	38200
Chromium	44	6
Copper	59	1
Lead	18	<1
Magnesium	2208	3400
Manganese	696	38
Selenium	<0.05	<1
Silver	<0.05	<1
Vanadium	29	2
Zinc	137	6
Sodium	4661	165
Nutrients: (mg/kg)		
TKN	842	<100
Phosphorous	54	73
Potassium	280	244

nd = not detected
na = not analyzed

4.2.2 Sludge

The sludge background information was determined by analyzing two samples taken from two of the 19 drums that contained the sludge used in this study. The sludge was analyzed for the same chemical parameters as the soil (analytical results are listed in Table 4.1. and represent the average of two samples). The O&G and moisture content were 25% and 48% respectively. The sludge contained toxic metals such as lead (18ppm), barium (123ppm), and chromium (44ppm). An analysis to determine the GAB

in the sludge was not conducted because GAB was not expected to be present in a sludge that was accumulated at the bottom of a crude tank closed for more than seven years.

An essential step in the analysis of tars and crude oils is their group type separation into saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltene fractions, a procedure commonly referred to as SARA analysis. This separation was conducted on the original sludge in order to determine the relative concentration of each of these four groups. The results showed that the weight percentage of the saturated hydrocarbons was 35.05%; aromatic hydrocarbons, 49.4%; resins 8.17%; and asphaltene fractions, 7.37%.

The gas chromatogram of the original sludge used in this study is shown in Figure 4.2. The chromatogram detected n-alkanes with a distribution from nC_9 to nC_{35}. This analysis provided background information on the main hydrocarbon components of the original sludge and helped in the assessment of the relative degree of biodegradation in the soil from all cells.

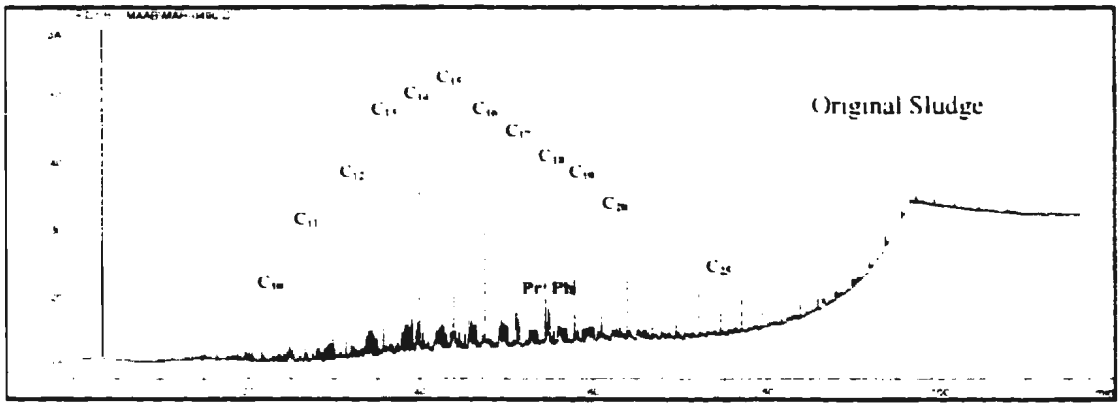

Figure 4.2 Gas chromatograph of original sludge sample used in the landfarm study

4.3 General Evaluation of Degradation Process

One of the objectives of this research was to study the biodegradation mechanisms of oily sludge. The two most widely used parameters for measuring the biodegradation of petroleum hydrocarbons, as reported in the literature, are O&G and Total Petroleum Hydrocarbons (TPH) (Huesemann 1995). While O&G is a measure of non-polar and polar hydrocarbons present in petroleum waste, TPH is a measure of non-polar hydrocarbons present in petroleum waste. For this study, O&G was the parameter used and Freon 113 was the solvent used for the extraction. The extract was measured by an Infrared (IR) instrument.

4.3.1 Decrease in Oil & Grease Levels

The mean O&G concentration for every cell taken on a monthly basis is listed in Table 4.2. Each concentration represents the average of three measurements. The mean O&G concentrations were also plotted against time (Figure 4.3a shows all landfarm cells and Figure 4.3b shows all bioreactor cells).

While evaluating Table 4.2 and Figures 4.3a and 4.3b, the following points were noted:

1- There is randomness in the reported concentrations. This was expected due to the nature of this study (field study, sampling method and analytical procedures).

2- There are three clear distinctive phases representing changes in the O&G concentrations in all cells. The first phase took place between day 1 and day 171. This period occurred in the fall and winter seasons. During this phase, a decrease in the O&G was apparent; however, it was not significant. In the second phase,

which took place between days 171 and 254, the drop in O&G concentrations was significant. This phase occurred during the spring season. In the third phase, which took place between day 254 and 348, there was hardly any drop in O&G concentrations. In fact, many of the cells showed a slight increase. This phase took place during the summer season.

3- The cells that were expected to show the highest decrease in O&G (LF5, BR2 & BR3) as a result of receiving optimal treatment conditions (tilling/aeration, addition of water and nutrient) did not do so compared to cells that received a partial treatment (LF2 only received tilling and LF3 received tilling and watering). While the cells that were expected to show the worse performance (LF1 & BR4, as they received no treatment at all) showed a greater decrease in O&G than LF4 which received tilling and nutrients (Figure 4.4).

4. This unexpected cell performance could not be attributed to biological processes alone, but could possibly be due to a combination of biological and physical processes. The physical process, referred to in this study as weathering, includes evaporation and wind stripping.

The initial and final levels of O&G for every cell were plotted as bar graphs (Figure 4.4). Due to variability in the data, and in order to minimize the error in calculating the total loss in each cell, it was decided to plot the bar graphs using the average of the first and last three data sets. The first bar (for each cell) represents the average of the first three data sets collected in September, October, and November 2000, and the second bar represents the average of the last three data sets collected in July, August, and September

2001. The decrease in O&G concentration in all cells is well demonstrated in this figure. The greatest decrease was at LF2 (76%) followed by LF5 (75%) and LF3 (71%), while the lowest decrease (40%) was at LF4. Another attempt was made to calculate the total loss based on calculating the average of the first and last two data sets. The difference in the total O&G loss between the two attempts was small and ranged from 1% to 2.5%.

Table 4.2 Mean O&G concentrations (mg/kg) for all cells

Date	LF1	LF2	LF3	LF4	LF5	LF8	BR2	BR3	BR4
9/26/2000	134747	103978	102775	83280	102373	181770	87040	89628	91775
10/24/2000	110313	104480	114467	49307	117380	156143	75597	75450	87690
11/26/2000	115295	108505	97370	63550	99005	152735	89235	76485	89675
12/17/2000	115040	77815	67060	86795	89435	148485	79185	82470	95465
1/9/2001	113970	89340	89610	55850	79125	151540	81680	76960	84700
2/3/2001	113270	68500	100790	66460	60770	147700	54550	63730	91300
3/11/2001	100175	62180	75275	64520	66975	158620	70700	63655	93770
4/9/2001	80330	23675	69725	45210	35760	128755	53210	70365	71425
5/7/2001	67250	45750	27683	28223	35125	105655	19640	22395	29063
6/2/2001	44770	13643	25320	20033	23190	72377	25700	28920	37403
7/8/2001	47680	24207	33680	38230	23703	69817	25147	28203	29433
8/5/2001	49287	26740	26860	41255	29280	70830	27435	25365	31360
9/4/2001	57480	24270	31387	37290	27033	67097	25430	25395	32400

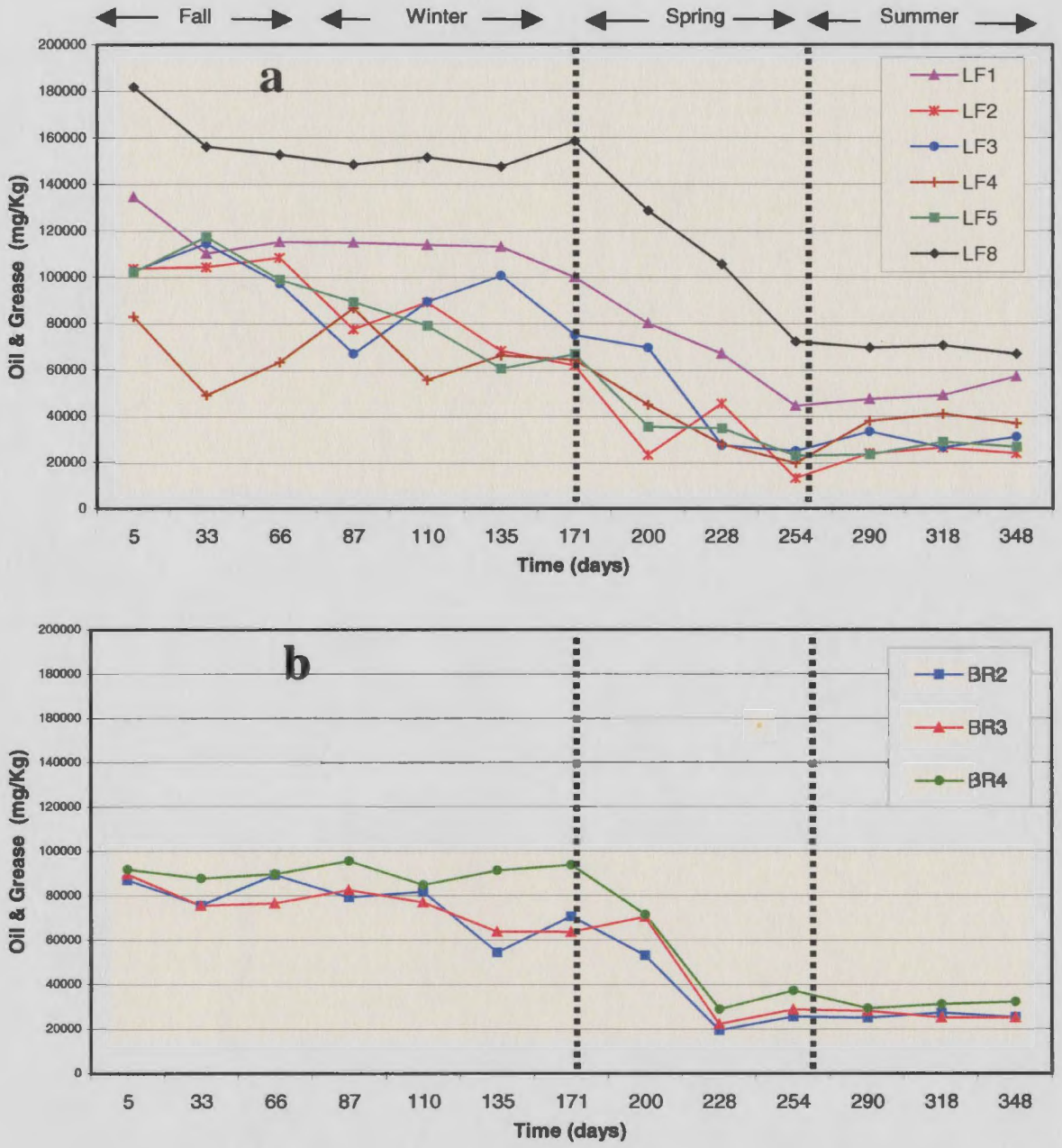

Figure 4.3 Mean O&G concentrations versus time: (a) landfarm and (b) bioreactor cells

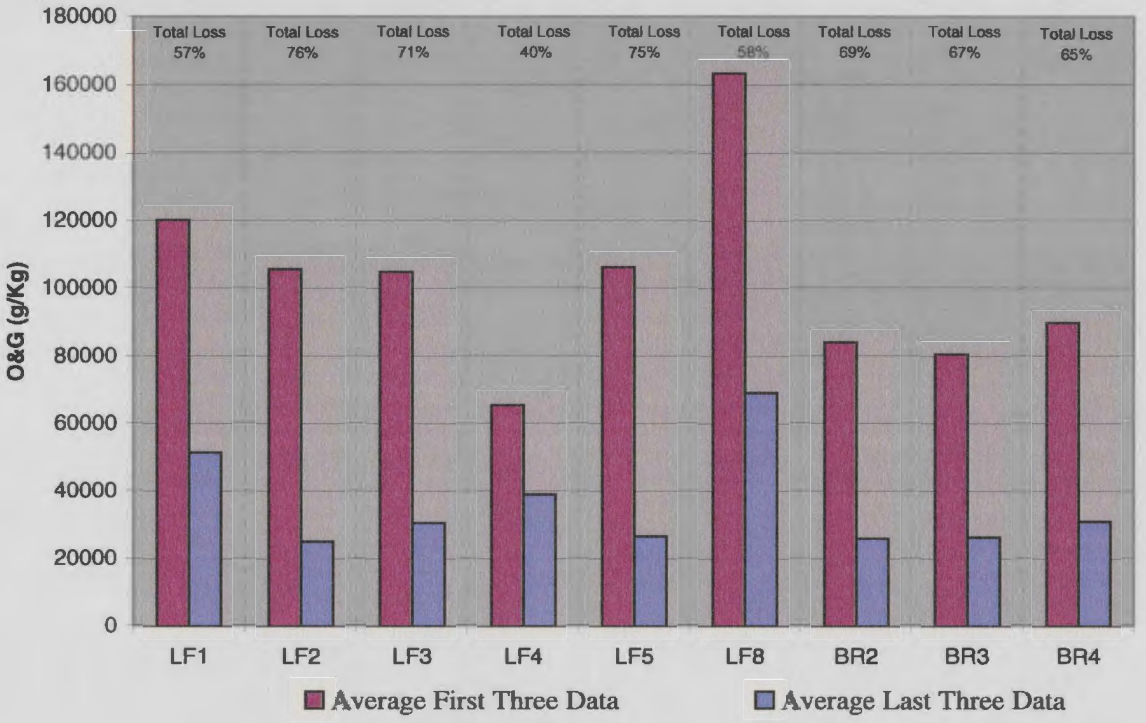

Figure 4.4 Bar graphs showing initial and final O&G levels for all cells

4.3.2 Effects of Biodegradation

The original plan of this research was to study the mechanisms of oily sludge biodegradation by measuring the O&G concentrations; however, the performance of the cells was not as expected, and, as a result, it was decided to analyze the aliphatic class of hydrocarbons. This class was chosen becaus it has one of the highest biodegradation potentials among all classes. Moldowan et al. (1992) and Chosson et al. (1992) proposed the following sequence for the selective biodegradation of hydrocarbon compounds by microorganisms: n-alkanes, isoprenoids, steranes, hopanes/diasteranes, aromatic steroids, and porphyrins. Huesemann (1994) summarized the relative biodegradation potential of major petroleum compound classes, with the following sequence: mono-aromatics, straight-chain alkanes, branched alkanes, saturated cyclics, polynuclear aromatics, and

polars. The aliphatic class consists of normal, branched and cyclic alkanes. Since measuring all the compounds within this class is time-consuming, and was not the objective of this study, it was decided to determine specific compounds that are known to be good indicators for the extent of biodegradation. Four compounds were used to assess the relative degree of biodegradation: two straight-chain alkanes (nC_{17} and nC_{18}) that can be easily biodegraded, and two multi-branched acyclic isoprenoids (pristane and phytane) that are relatively more resistant to biodegradation than their normal alkane counterparts.

Peters and Moldowan (1993) provided a guide to rank the extent of crude oil biodegradation based on the analysis of various compound classes. On a scale of 1 to 10 (light to severe biodegradation) the partial destruction of the normal paraffins signifies light biodegradation (scale of 1 to 2), whereas their complete destruction corresponds to a scale of 3. The onset of the destruction of the isoprenoids (i.e., pristane and phytane) indicates a moderate level of biodegradation (scale of 4 to 5) and their complete removal indicates heavy biodegradation (scale of 6). Evaluation of the biodegradation beyond 6 requires analysis of other biomarkers referred to as hopanes and steranes. These are detected using GC-MS analysis. The hopanes and steranes are cyclic alkanes known as naphthenes, and they are one of the most resistant hydrocarbons to biodegradation.

Field treatments for the nine cells varied from natural attenuation (LF1), to treatments using various degrees of tilling, watering, aeration and nutrients (LF2 to LF8), and the use of a bioreactor (BR2 through BR4). For each cell, four samples were collected over a period of one year (October/00, February/01, May/01 and September/01) and were

analyzed using GC-FID. The GC-FID chromatograms show a clear trend of n-alkane biodegradation. As biodegradation proceeded, the normal alkanes were preferentially degraded. The chromatograms for the nine cells showed various degrees of biodegradation over time. Not surprisingly, the samples that were left for natural attenuation (LF1 and BR4) showed the least effects of biodegradation (Sections 4.6.1 and 4.6.9). In contrast, treatments using tilling, watering and nutrients (LF5) showed a significant reduction in the amount of the normal alkanes over time (Section 4.6.5). The level of biodegradation in the nine cells, according to Peters and Moldowan (1993) guide, ranged from light (1) to moderate (4).

The degree of biodegradation was determined using the ratios of n-C17 to pristane and n-C18 to phytane (Chen 1994). The chromatographic peak area counts of the two straight-chain alkanes (nC_{17} and nC_{18}) and the two multi-branched acyclic isoprenoid (pristane and phytane) compounds for each sample along with the computed nC_{17}/Pr and nC_{18}/Ph ratios are listed in Table 4.3. Figure 4.5 shows the plot of nC_{17}/Pr versus nC_{18}/Ph for the samples. For easier comparison, the samples are plotted as two groups: Figure 4.5a shows the least biodegraded (LF1, LF2, LF3, and BR4), and Figure 4.5b the most biodegraded (LF4, LF5, LF8, BR2, and BR3) samples. Figure 4.5a shows only minor differences in the nC_{17}/Pr and nC_{18}/Ph ratios, and hence the relative degree of biodegradation among the samples. Figure 4.5b shows a significant progression in the relative degree of biodegradation for each treatment over time.

When the values of these two ratios decrease simultaneously, they indicate that n-C17 and n-C18 are being preferentially biodegraded because pristane and phytane are more resistant to biodegradation. The relative concentration (ratio) of the two compound classes (nC_{17}/Pr and nC_{18}/Ph) was used to assess the relative degree of biodegradation among samples that are slightly to moderately biodegradable (Christiansen et al., 1993; Peters and Moldowan 1993; Chen 1994; Wang et al. 1995; Douglas et al. 1996).

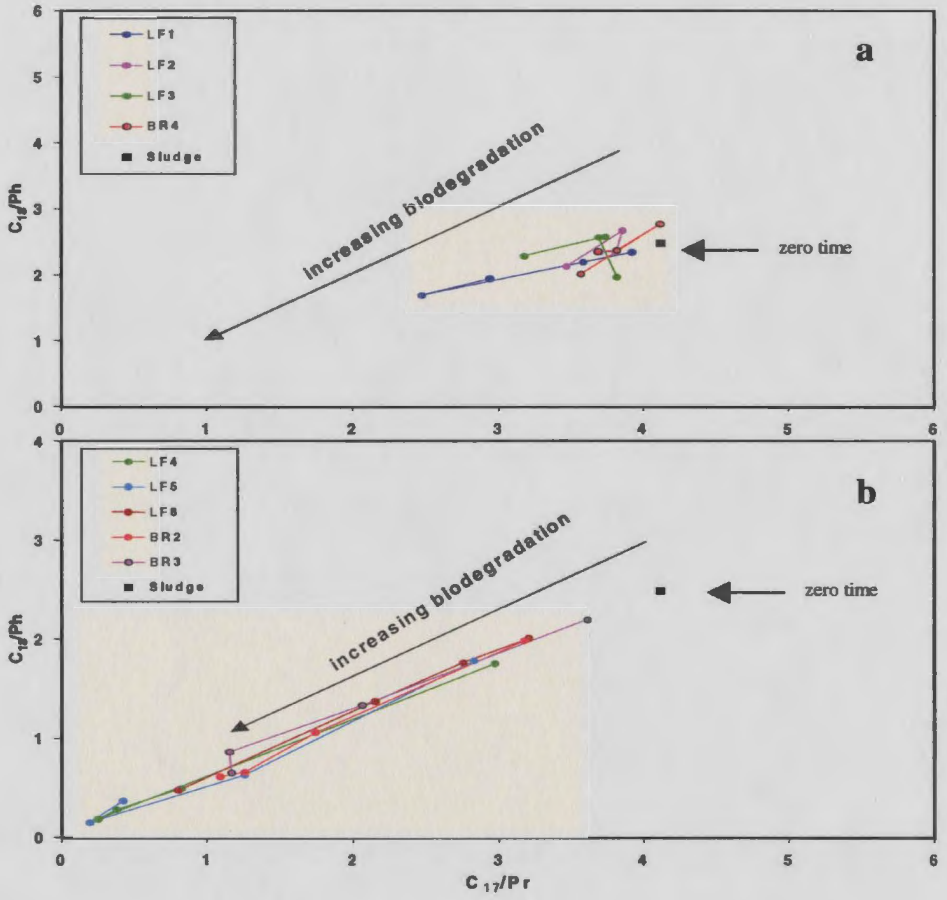

Figure 4.5 C_{17}/Pr versus C_{18}/Ph for the least biodegraded (a) and most biodegraded (b) samples.

Table 4.3 Chromatographic peak area counts for C17 and C18 n-alkanes and for Pristane and Phytane Isoprenoids

Landfarm site	Date collected	nC_{17}/Pr	nC_{18}/Ph	nC_{17}	Pristane	nC_{18}	Phytane
Sludge	09/07/00	4.12	2.49	171.25	41.58	141.83	56.96
LF1	10/24/00	3.59	2.2	67.35	18.77	54.76	24.85
LF1	02/03/01	3.92	2.35	62.9	16.05	51.51	21.91
LF1	05/07/01	2.48	1.7	49.55	19.95	39.73	23.34
LF1	09/04/01	2.95	1.95	84.19	28.57	70.49	36.1
LF2	10/24/00	3.47	2.14	28.69	8.27	22.87	10.68
LF2	02/03/01	3.86	2.68	33.72	8.74	27.62	10.3
LF2	05/07/01	3.81	2.37	33.65	8.83	28.67	12.12
LF2	09/04/01	3.7	2.36	19.87	5.37	16.66	7.06
LF3	10/24/00	3.81	1.98	41.11	10.78	33.67	16.99
LF3	02/03/01	3.69	2.58	40.1	10.86	32.95	12.78
LF3	05/07/01	3.74	2.58	45.94	12.29	39.39	15.24
LF3	09/04/01	3.18	2.29	27.24	8.56	23.36	10.19
LF4	10/24/00	2.97	1.75	25.69	8.64	20.74	11.82
LF4	02/03/01	0.26	0.2	1.12	4.39	1.52	7.69
LF4	05/07/01	0.39	0.29	1.62	4.18	2.2	7.55
LF4	09/04/01	0.83	0.51	12.37	14.97	10.36	20.51
LF5	10/24/00	2.83	1.78	84.04	29.68	68.92	38.65
LF5	02/03/01	1.26	0.64	7.88	6.24	6.09	9.57
LF5	05/07/01	0.2	0.17	1.05	5.24	1.72	10.35
LF5	09/04/01	0.43	0.38	1.06	2.49	1.73	4.57
LF8	10/24/00	3.21	2.01	92.62	28.86	74.74	37.18
LF8	02/03/01	2.76	1.76	50.33	18.26	42.34	24.04
LF8	05/07/01	2.15	1.38	39.38	18.29	32.75	23.76
LF8	09/04/01	0.81	0.49	13.57	16.75	11.23	23.13
BR2	10/24/00	3.18	1.99	40.84	12.85	33.61	16.92
BR2	02/03/01	1.75	1.07	10.9	6.24	8.87	8.31
BR2	05/07/01	1.27	0.67	8.31	6.56	6.63	9.88
BR2	09/04/01	1.1	0.62	5.61	5.11	4.4	7.07
BR3	10/24/00	3.61	2.2	37.19	10.3	30.47	13.88
BR3	02/03/01	2.06	1.34	18.76	9.09	16.21	12.12
BR3	05/07/01	1.16	0.87	8.22	7.1	9.63	11.09
BR3	09/04/01	1.17	0.66	6.15	5.25	4.62	6.99
BR4	10/24/00	3.57	2.02	64.62	18.11	52.06	25.74
BR4	02/03/01	4.11	2.78	26.19	6.37	21.27	7.65
BR4	05/07/01	3.82	2.38	69.06	18.1	56.2	23.61
BR4	09/04/01	3.69	2.36	70.2	19.04	58.26	24.66

4.3.3 Effects of Weathering

Salanitro (2001), in his review of the literature on the biodegradability of petroleum hydrocarbons, stated that declines in bulk petroleum hydrocarbons in soils in laboratory and field experiments are the result of volatilization and biodegradation. Salanitro also noted that most of the reported studies only assessed the bioremediation potential of petroleum hydrocarbons without accounting for mass removal due to weathering and evaporation.

Two observations from the results of the present study supported Salanitro's statements that the decrease in hydrocarbon in the soil is due to two processes: biodegradation and weathering. The first was the unexpected performance of some cells such as LF1 and LF2 compared to LF4 and LF5. The first two cells showed a greater decrease in the O&G concentrations (57% and 76%, respectively) compared to the last two (40% and 75%). This was unexpected because LF1 had no treatment compared to LF4 which had partial treatment, and LF2 received tilling, while LF5 received both tilling, watering and nutrients. The second observation is that cells such as LF4 that showed the least decrease in O&G concentration had the most significant reduction in its n-alkanes, while cells such as LF2 that had hardly any decrease in its n-alkanes components showed the maximum decrease in its O&G concentration.

From the above two observations, it can be concluded that biodegradation was not the only process responsible for the loss of hydrocarbons and that the weathering process,

which is mainly due to evaporation, played a major role in the degradation of hydrocarbons in this study.

Weathering, unlike biodegradation, does not have any preferential depletion between normal hydrocarbons and their branched counterparts since both have the same boiling points. However, the light end hydrocarbons with boiling points of 220°C or less tend to evaporate faster. These light end hydrocarbons correspond to $\leq$ C12.

The maximum air temperature recorded at the site was 46°C (Table 4.4 lists the monthly air temperatures in the site). The temperature of the soil was measured at different times and dates in order to determine the difference between soil and air temperatures. The results showed that the soil temperature was approximately 6°C higher than the air temperature. The temperature starts rising in the Juaymah area in the spring. Between April and June 2001, the average soil temperature was between 32°C and 39°C.

When the moisture content data were evaluated, it was noticed that starting in April 2001, (April represents the beginning of the hot season in Saudi Arabia) the moisture content in all cells (Table 4.4) started to decrease despite the weekly watering (Figures 4.6a & 4.6b). This can mainly be attributed to the effect of evaporation (yearly evaporation rate in the study area is approximately 86 inches), which is caused by the high temperature. The O&G data also showed that concentrations of O&G started to decrease more rapidly in April (Figure 4.3). Both decreases in moisture content and O&G took place six months after the sludge was applied to the cells. As for the drop in the O&G levels, this was

attributed to biological and or weathering processes. Cells that did not show any sign of biodegradation (n-alkanes were intact) throughout this study (LF1, LF2, LF3, and BR4) showed a large drop in their O&G concentrations. This drop also started in April. In addition, the calculated nC17/Pr and nC18/Ph ratios for these four cells hardly had any changes throughout this study (Table 4.3). All of this indicates that when the high temperature season started (April), evaporation not biodegradation was the dominant degradation process. Another indication that evaporation was the dominant process is the presence of both pristane & C17 and phytane & C18. These have virtually the same boiling points, which means that if evaporation took place, both would have been affected in the same way.

Table 4.4 Soil moisture contents and climatic conditions

Soil Moisture Content (%)

Cell Number	9/26/00	10/24/00	11/26/00	12/17/00	1/9/01	2/3/01	3/11/01	4/9/01	5/7/01	6/2/01	7/8/01	8/5/01	9/4/01
LF1	6.4	3.7	9.7	8.2	8.9	8.9	6.6	3.6	4.5	4.1	3.8	3.0	3.4
LF2	4.8	4.3	7.3	5.3	6.9	4.9	3.0	1.9	2.2	1.3	1.6	1.6	1.4
LF3	5.4	5.3	8.4	6.0	8.1	5.3	7.0	4.6	3.5	2.1	2.1	1.8	2.0
LF4	4.0	2.4	5.4	8.5	5.4	4.2	3.9	3.5	2.7	1.3	2.1	2.4	1.9
LF5	5.5	4.8	8.5	10.6	8.1	5.9	9.3	6.2	5.0	3.2	1.7	2.6	3.3
LF8	11.4	8.0	10.2	9.1	10.0	10.2	9.1	8.3	9.6	8.6	7.4	7.0	7.7
BR2	5.9	3.7	7.6	7.6	9.9	7.7	10.5	10.0	7.2	6.2	5.1	3.9	3.2
BR3	5.2	4.6	7.5	9.6	7.1	5.9	6.9	5.6	5.8	4.1	2.8	2.1	1.7
BR4	7.3	4.7	4.8	4.9	6.7	9.4	4.9	3.6	3.8	3.6	2.4	2.5	2.2

Temperature (°C) and Rainfall (mm) Data

Months	Sep	Oct	Nov	Dec	Jan	Feb	March	April	May	June	July	Aug	Sep
Max Temp	44.7	38.1	32.7	26.2	22.4	26.2	32.8	39.6	41.4	40.9	45.7	44.9	43.2
Min Temp	24.1	19.8	14.7	9.4	7.6	8.2	14.7	17.0	22.1	24.9	26.9	28.1	24.8
Mean Temp	31.9	28.7	21.8	18.6	15.5	17.0	21.1	26.1	30.4	32.7	34.8	34.9	32.9
Rainfall			82.9	9.9									

As for the biodegradation process, evaluation of the GC-FID data for the cells that had a significant reduction in the n-alkanes (LF4 and LF5) showed that these reductions took place at an earlier stage (prior to April), as can be seen from the decrease in the nC17/Pr and nC18/Ph ratios (Table 4.3). This again supports the conclusion that evaporation was the predominant process during the hot season.

The cover on the BR2 cell minimized the effect of evaporation compared to the uncovered cells. Moisture content measurements from BR2 (covered) and BR3 (no cover) showed that during the summer season, BR2 had approximately 46% more moisture than BR3. This shows that the cover was effective in minimizing the evaporation process.

As for the effect of wind action, BR2 and BR3 had exactly the same treatment. However, BR2 had a cover, while BR3 had no cover. The O&G drop in BR2 was 69%; in BR3 it was 67%. Since both cells were at the same temperature and since BR2 showed a greater drop in O&G than BR3 (2%), it can be concluded that evaporation was the predominant process and the wind action had no effect.

Another observation related to evaporation can be concluded from LF4. This cell showed the smallest drop in O&G levels (40%) compared to other cells. This means that evaporation was not high even though the cell was among those that had the most significant reduction in n-alkanes. The reason for this small reduction in the level of O&G is that the addition of fertilizers without the addition of water caused the soil to

become more compacted (this was evidenced by the hardness of the soil when auguring) and acted as a cover and minimized the evaporation affect. The fertilizer also reduced the porosity of the soil, allowing it to retain a higher moisture content as evidenced by the presence of almost the same moisture content in LF4 (not watered) and LF3 (watered on a regular basis). During the last three months of this study (July, August, and September 2001), the moisture content in LF4 was 2.1, 2.4 and 1.9, respectively, and for LF3, it was 2.1, 1.8 and 2.2, respectively.

4.3.4 Effects of Leaching

As discussed in Section 3.2.2, leaching was not expected to take place. This was also supported by other researchers (Kincannon 1972; Raymond et al. 1976; Dibble and Bartha 1979b;). Therefore, the focus of this study was mainly on the biodegradation and weathering processes. However, to ensure that leaching was not taking place, samples were collected from depths between 6 to 12 inches below the landfarm cells and were analyzed to see if the O&G concentrations at this depth were increasing with time. An increase in the concentrations at this depth would indicate that leaching was occurring. Table 4.5 lists the O&G concentrations from samples collected on October 24, 2000 (just one month after the sludge was applied to the cells) and on March 11, 2001 (just after the end of the rainy season). These results clearly show that the O&G concentrations decreased in all the cells (except LF2 and LF3 where the O&G levels slightly increased) and indicate that leaching did not occur. A comparison of the O&G levels between the top and bottom layers also indicated that O&G was mainly confined in the top layer.

Table 4.5 Oil & Grease levels (mg/kg) obtained from depths between 0-6″ and 6-12″

Date	Depth	LF1	LF2	LF3	LF4	LF5	LF8
10/24/2000	0-6″	110313	104480	114467	49307	117380	156143
	6-12″	9450	4335	5687	15385	9330	82530
3/11/2001	0-6″	100175	62180	75275	64520	66975	158620
	6-12″	5800	5460	6020	7350	4035	70030

4.3.5 Evaluating Parameters Influencing Degradation Process

Various parameters that influence the degradation processes include: moisture content, microbes, nutrients, pH, and aeration. These parameters are briefly discussed in the following sections.

4.3.5.1 *Moisture Content*

The water content of the soil (especially when extremely high or low) can influence the rate of biodegradation. Too much water will hinder the supply of oxygen and as a result will decrease the rate of biodegradation (Concawe 1980). On the other hand, little water will inhibit microbial activities. The water-holding capacity for the cells was determined in order to decide if the added water was sufficient to support microbial activity. A laboratory experiment similar to the one done for the sand (see Section 4.2.1) was conducted on a soil sample obtained from LF2 (Appendix B). The average water-holding capacity for the soil was 5.5%. If the same principle for calculating the optimal water for supporting the microbes (Huesemann 1994) is applied here, this means that the microorganisms will require a soil moisture content between 1.6% and 4.9%.

The soil moisture inside the cells came from three sources: water in the original sludge (49% of the sludge was water), the rain that occurred between November and December 2000 (92 mm), and the water added to cells LF3, LF5, LF8, BR2 and BR4 on a regular basis (55 liters/week/cell) during the study period. Table 4.4 lists the measured water content during this study. A laboratory test was conducted in order to determine if the measured moisture content was only water origin or if it included any hydrocarbon components that could have evaporated during the moisture content experimental test. The results showed that the measured moisture content was only water origin and did not include any hydrocarbon constituents. Detailed experimental procedures and results are listed in Appendix B. The moisture contents for all landfarm and bioreactor cells were plotted against time (Figures 4.6a and 4.6b, respectively). Both figures show that the moisture contents in all cells were within the required range (1.6% and 4.9%) throughout the study period, which meant that the cells had enough water to support microbial activities. Table 4.4 also shows that watering the cells did not make any significant contribution to the biodegradation process. Cells that were not watered (LF1, LF2, LF4, & BR4) contained enough moisture (moisture from original sludge) to sustain the microbial activities as supported by the microbial counts from Table 4.6. The microbial counts in these cells were as high as those in the watered cells. The moisture content in LF1 (no tilling) and BR4 (capped) were higher than cells that were watered and tilled (LF2, LF5, and BR3). During the fieldwork, it was also noticed that the added water evaporated almost immediately. The high temperature and tilling contributed to the high evaporation rate in the cells. The moisture content in LF8 (higher oil content) was higher than any of the other cells. It appears that the high oil content kept the moisture more

intact and minimized its evaporative losses. In general, it can be concluded that adding water to the cells did not make a significant difference in terms of microbial counts or activities as a result of the presence of a high moisture content in the original sludge.

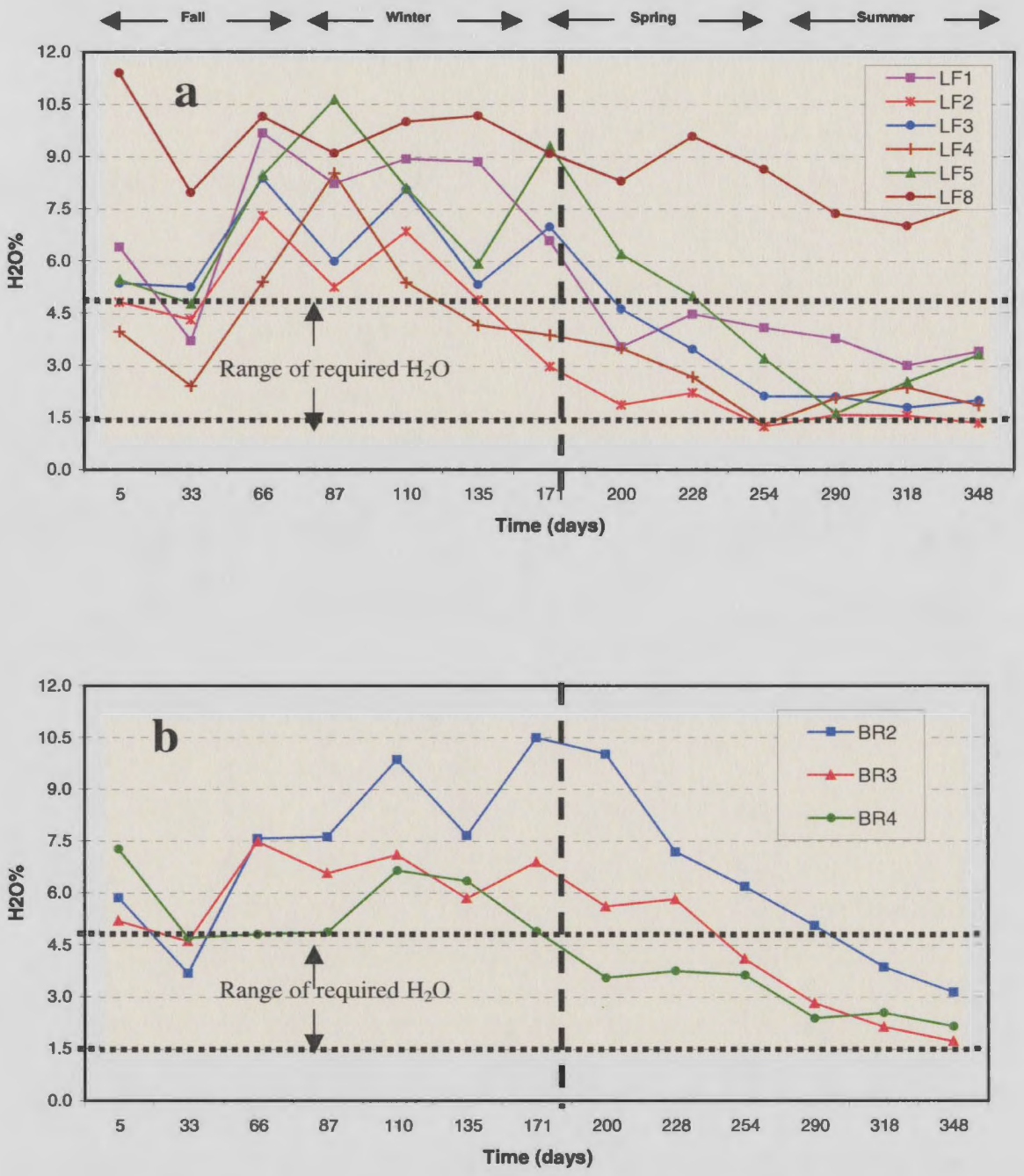

Figure 4.6 Moisture content versus time: (a) landfarm and (b) bioreactor cells

4.3.5.2 *Microbes*

The microbial counts in all cells were between 10^5 and 10^{12} microbial cells per gram (Table 4.6). This range is within the range recommended in the literature (Morgan, et al., 1989 and Arora, et al., 1982). The primary microbial species that was identified in the soil inside the cells is known as *Burkholderia Glumae* (the bacterial identification results are shown in Appendix C). *Burkholderia Glumae* is one of the microbes known to be responsible for the biodegradation of hydrocarbons (Da Cunha, et al., 2000, Balashova et al., 1999 and Salanitro, 2001). The microbial counts reached their peaks in most cells (BR2, BR3, BR4, LF4 and LF8) during the month of March (Figures 4.7). A sharp drop in the microbial counts occurred between April and May. This drop coincides with the drop in the moisture content (Section 4.3.5.1) in the cells and the beginning of the hot season. After this drop, the bacterial counts remained almost constant throughout the remainder of the study period.

Table 4.6 General Aerobic Bacteria (GAB/g)

Cell Number	9/26/00	10/24/00	11/26/00	12/17/00	1/9/01	2/3/01	3/11/01	4/9/01	5/7/01	6/2/01	7/8/01	8/5/01	9/4/01
LF1	4.3E+07	2.1E+08	9.2E+06	8.5E+07	9.2E+08	2.2E+10	7.2E+06	1.6E+07	9.1E+06	1.4E+08	2.2E+06	3.9E+06	4.0E+07
LF2	2.3E+08	4.0E+07	4.2E+07	1.4E+08	1.5E+08	8.8E+07	4.0E+07	4.4E+06	1.9E+05	8.5E+04	3.9E+05	2.1E+06	3.9E+06
LF3	7.5E+06	2.2E+08	9.1E+08	4.1E+07	9.1E+08	8.8E+08	1.4E+08	4.5E+06	1.3E+07	3.9E+06	3.9E+05	2.1E+06	2.1E+07
LF4	4.3E+07	4.0E+07	2.2E+10	2.1E+08	9.1E+08	2.1E+10	2.1E+12	7.8E+07	4.0E+07	1.4E+07	3.9E+06	3.9E+06	3.9E+07
LF5	2.3E+08	2.2E+08	4.2E+09	1.5E+09	2.3E+10	2.1E+10	9.2E+08	1.6E+08	8.8E+07	4.0E+06	3.9E+05	8.5E+07	8.7E+08
LF8	2.3E+05	2.2E+08	4.3E+08	4.3E+08	2.3E+09	2.3E+09	2.3E+12	4.7E+06	1.5E+07	9.2E+06	9.0E+07	1.4E+07	4.2E+09
BR2	2.3E+08	2.1E+08	1.5E+09	9.1E+08	2.3E+10	2.2E+10	2.3E+12	2.6E+07	4.2E+07	8.9E+08	8.8E+07	4.0E+07	2.1E+07
BR3	2.3E+07	2.2E+08	9.0E+08	4.1E+09	4.3E+08	2.2E+10	2.2E+12	4.6E+07	4.1E+07	8.7E+08	2.1E+07	2.1E+07	2.1E+06
BR4	2.3E+07	2.2E+08	2.2E+10	2.2E+08	4.1E+08	2.2E+10	2.1E+12	9.6E+06	4.0E+05	4.0E+06	3.9E+05	3.9E+06	2.1E+07

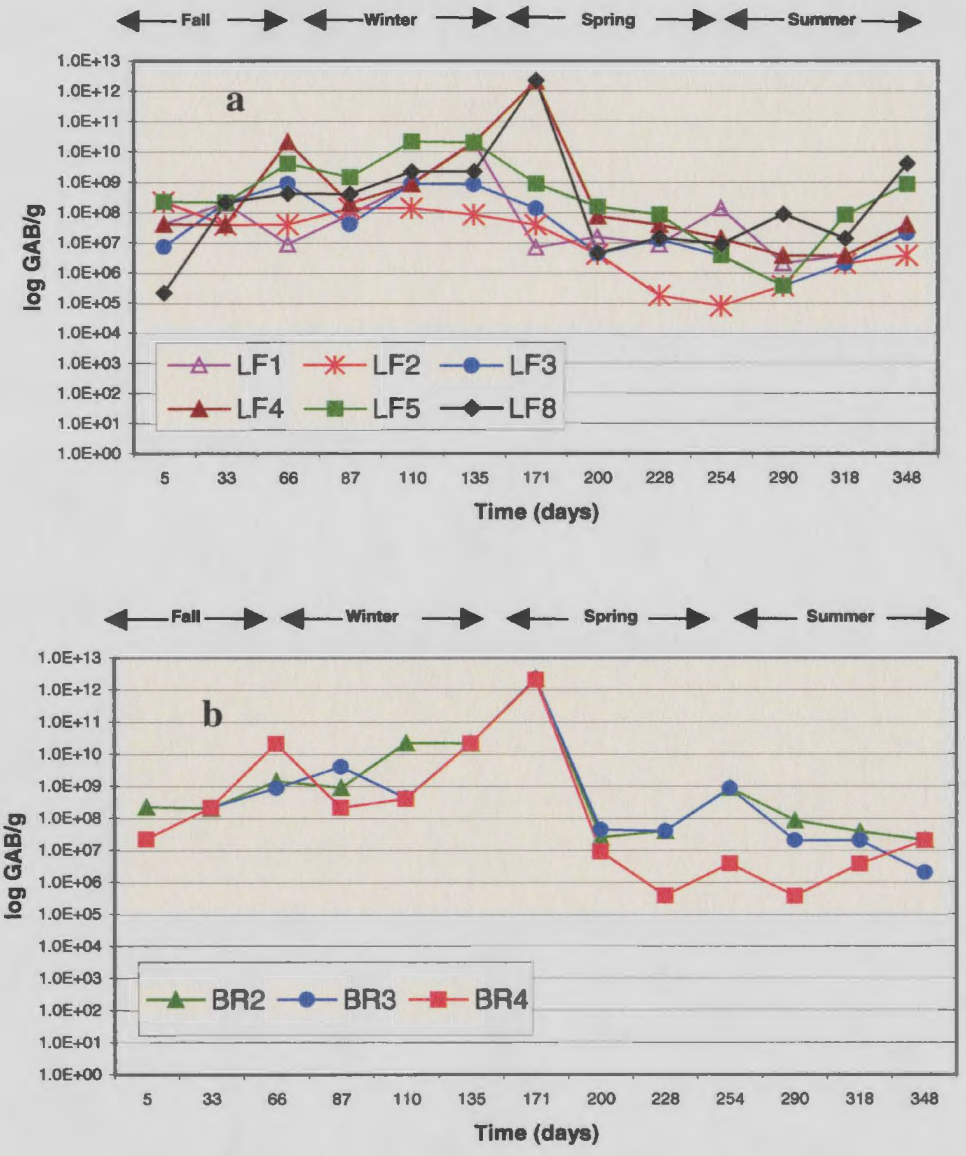

Figure 4.7 Microbial distributions versus time: (a) landfarm and (b) bioreactor cells

4.3.5.3 *Nutrients*

For the conversion of the hydrocarbons to biomass, three elements are required: nitrogen, phosphorus and potassium. Other elements such as zinc, calcium, manganese, iron, and sulphur are also required in smaller quantities. The addition of normal agricultural

mineral fertilizers to landfarms generally increases the biological activity (Concawe 1980). During this study, nutrients and metals were measured on three dates: at the beginning (October 24, 2000), in the middle (March 11, 2001), and at the end of the study (September 4, 2001) (see Table 4.7).

Nitrogen can be available for the microbes in two forms: inorganic and organic. The inorganic nitrogen (nitrate, nitrite, and ammonia) can be supplied as fertilizer; the organic nitrogen includes material such as proteins, peptides, nucleic acids, urea and numerous synthetic compounds and can be supplied in the form of fertilizer as well as plant matter and oil. The Saudi Aramco laboratory was not equipped to measure for nitrate and as a result, it was decided to measure for TKN, which is the combination of ammonia and organic nitrogen (LCRA 2001). The purpose of this study was to measure the effect of adding nutrients to some cells and not to determine the optimal amount required. Still, the TKN was used in this study as an indicator for the activities of the microbes. Greater TKN values would mean more microbial activity; on the other hand, if there was no microbial growth, then all the nitrogen would remain the same. The cells where fertilizer was added (LF4, LF5, LF8, BR2, and BR3) showed higher TKN concentrations than those that did not receive fertilizer. It was also noted from the n-alkanes gas chromatography results that cells where nutrients were added were the only ones that showed a significant reduction of their n-alkanes. From this it can be concluded that nutrients played a major role in the biodegradation process by increasing the microbial activity, minimizing the weathering effect, and leading to the highest rate of biodegradation of n-alkanes.

Table 4.7 Metals and nutrients concentrations (mg/kg) in different landfarm cells

Metals	LF1			LF2			LF3			LF4			LF5		
	10/24/00	03/11/01	09/04/01	10/24/00	03/11/01	09/04/01	10/24/00	03/11/01	09/04/01	10/24/00	03/11/01	09/04/01	10/24/00	03/11/01	09/04/01
Arsenic	1.8	1.9	0.5	2.0	1.7	1.1	2.0	2.0	<0.4	1.1	1.8	<0.4	1.6	1.9	<0.4
Barium	36	42	43	36	39	29	38	41	29	25	39	36	30	44	29
Cadmium	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Calcium x1000	46	52	49	47	51	45	45	50	41	39	45	43	43	46	45
Chromium	22	18	13	17	17	12	17	18	6.0	12	16	12	15	18	9.1
Copper	12	11	15	10	11	8.0	12	13	9.3	6.5	10	12	9.6	12	9.5
Lead	7.0	5.9	5.4	4.6	4.8	2.9	5.5	4.5	3.1	4.3	6.1	3.5	4.8	5.7	2.8
Magnesium	3580	4340	3940	3790	3830	3520	3440	3690	3230	3490	3490	3480	3470	3590	3580
Manganese	186	182	210	167	156	133	164	178	138	114	157	160	149	177	144
Selenium	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Silver	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Vanadium	12	15	11	12	12	9.9	12	13	7.4	9.3	12	10	11	13	8.5
Zinc	23	23	30	20	18	17	22	21	18	12	19	23	20	23	19
Nutrients															
TKN	264	332	452	268	232	244	373	292	215	483	465	407	301	689	340
Phosphorous	98	89	91	91	90	88	81	82	76	99	78	88	91	100	99
Potassium	305	435	341	326	453	320	319	392	338	376	424	393	347	437	343

Metals	LF8			BR2			BR3			BR4					
	10/24/00	03/11/01	09/04/01	10/24/00	03/11/01	09/04/01	10/24/00	03/11/01	09/04/01	10/24/00	03/11/01	09/04/01			
Arsenic	2.2	2.6	0.9	1.2	1.4	<0.4	1.0	1.4	<0.4	1.5	0.5	<0.4			
Barium	48	59	47	26	27	24	23	26	25	30	26	26			
Cadmium	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2			
Calcium x1000	44	40	40	32	29	32	29	29	33	35	32	33			
Chromium	22	28	15	12	10	5.9	9.7	10	4.2	14	11	4.8			
Copper	19	19	19	8.2	9.1	7.4	7.5	8.8	8.2	8.9	7.7	9.1			
Lead	9.6	10.0	5.8	3.6	4.8	2.5	3.6	4.7	2.7	4.5	3.0	3.1			
Magnesium	2360	2270	2430	2520	2080	2150	1870	2040	2160	2770	2670	2740			
Manganese	213	232	210	108	104	105	100	100	105	134	118	125			
Selenium	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6			
Silver	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4			
Vanadium	12	14	10	5.9	5.8	6.6	5.0	5.7	6.3	7.0	4.8	7.3			
Zinc	42	61	41	15	15	16	22	14	18	17	20	17			
Nutrients															
TKN	802	908	713	476	397	295	546	290	495	345	255	248			
Phosphorous	82	94	82	67	46	80	57	42	59	72	19	65			
Potassium	254	274	230	293	284	254	256	284	227	299	342	313			

4.3.5.4 *pH*

The optimal pH required in a landfarm soil is between 6.5 and 8 (Arora et al. 1982; Morgan, et al., 1989; Huesemann 1994). If the pH is higher or lower than the above limits, microbial growth will be affected, and the soil chemistry will be modified. This could restrict the exchange of nutrients in the soil. The pH of the sand was high (9.6) and the pH of the original sludge was 7.2. When the study started, it was thought that there might be a need to do pH adjustment, but when the sand and sludge were mixed, the mixture pH was between 7.1 and 8.4. The pH of the soil inside the cells was monitored on a monthly basis (results are listed in Table 4.8) and the pH readings were stable in all cells throughout the research period, ranging between 6.4 and 8.4. Since the pH in all cells was within the recommended range, a pH adjustment was not necessary.

Table 4.8 pH measurements for all cells

Cell Number	9/26/00	10/24/00	11/26/00	12/17/00	1/9/01	2/3/01	3/11/01	4/9/01	5/7/01	6/2/01	7/8/01	8/5/01	9/4/01
LF1	8.3	7.8	7.5	7.6	7.4	7.1	7.2	7.9	7.7	7.2	7.0	7.0	7.8
LF2	8.4	7.9	7.7	7.8	7.5	7.3	7.1	8.0	8.2	7.6	7.3	7.0	8.0
LF3	8.4	7.8	7.9	7.8	7.4	7.4	7.1	7.8	8.1	7.6	7.1	6.7	7.7
LF4	7.2	8.0	7.9	7.6	7.6	7.4	7.2	7.6	7.7	7.2	6.5	6.4	7.4
LF5	7.9	7.9	7.7	7.7	7.6	7.5	7.2	7.6	7.9	7.2	7.0	7.3	7.5
LF8	7.8	8.1	7.5	7.5	7.5	7.1	7.2	7.7	7.7	7.1	7.0	7.4	7.8
BR2	7.1	7.8	7.5	7.6	7.7	7.1	7.7	7.8	8.0	7.6	7.4	7.6	8.1
BR3	7.4	7.8	7.5	7.7	7.8	7.2	7.8	7.8	7.8	7.5	7.3	7.3	7.7
BR4	7.7	7.9	7.7	7.7	7.5	8.0	7.7	7.8	8.1	7.5	7.4	7.4	7.7

4.3.5.5 *Tilling/Aeration*

Tilling/aeration plays a major role in the degradation process (Morgan and Watkinson 1989; Rast 1997). Unlike the other parameters (moisture content, microbes, nutrients, pH) where the data were physically measured and evaluated, tilling could not be

physically measured. As a result, the effect of tilling/aeration is being evaluated throughout the performance of the cells.

The two degradation processes that took place at the studied cells are biodegradation and weathering (Sections 4.3.2 and 4.3.3). The effect of tilling on the biodegradation process can be summarized as follows:

- It is the mechanism by which the oxygen essential for the growth and function of the aerobic microorganisms is introduced to the soil.
- It exposes the bacteria to fresh oil, which allows them to biodegrade more hydrocarbons.

The effect of tilling on the weathering process can be summarized as follows:

- It increases the mechanism of volatilization.
- It provides proper mixing (for even distribution of hydrocarbon in the soil).
- It replenishes the voids and exposes new oil to the surface.
- It disturbs the whole soil setting, causing a change in the oil/solid interface.

In this study, tilling was applied once a week to landfarm cells LF2, LF3, LF4, LF5, and LF8. When the reduction in the O&G levels among these five cells was compared, it was observed that the highest decrease (76%) occurred in cell LF2, which was only tilled. Cells that received tilling in addition to other treatments showed less reduction in their O&G levels. This clearly indicates that tilling played a significant role in the degradation process.

Huesemann (1994) stated that more frequent tilling might not be advantageous because it could have a negative effect on the soil structure (particularly in wet soils) and enhance soil water evaporation. In this study, where the climate is considered as arid and hot, frequent tilling alone resulted in the highest reduction in O&G levels as a result of weathering (volatilization) without causing any negative effect on the soil structure. This shows that operating parameters can play different roles under different climatic conditions.

Air was mechanically injected in bioreactor cells BR2 and BR3. When the performance of these two cells was compared with that of LF5 (LF5 had similar treatments except that aeration was applied by tilling), the results showed that LF5 out-performed the bioreactor cells in total O&G reduction. The relatively low reduction in the O&G in BR2 and BR3 is believed to be due to mechanical aeration, which did not disturb the soil structure except near the path that the air followed. Mechanical aeration also did not expose the bottom layers of hydrocarbons to the top surface, thus resulting in relatively lower weathering effects.

From this it can be concluded that tilling is the most important parameter that affects the degradation process in arid regions. It can also be concluded that aeration through tilling is more effective than mechanical aeration.

4.4 Evaluation of Hydrocarbon Degradation Using Open System Pyrolysis

Another analytical method known as Open System Pyrolysis was used in this study. This method has not been used or referred to in the literature for studying the biodegradation of oily waste. Various commercially available instruments utilize the method of Open System Pyrolysis. The most widely used instrument known as Rock-Eval, was developed by the Institute Français du Petrole (IFP) for petroleum exploration in the early 1980s. This particular study used the Rock-Eval-6, the most advanced version of this instrument, which uses a Flame Ionization Detector (FID) and Infra Red Detector and has two main components: a pyrolysis oven and an oxidation oven. In the pyrolysis oven, the instrument uses temperature-programmed heating to heat a small amount of sample (100 mg), from 210°C to 630°C in an inert atmosphere (helium or nitrogen), in order to determine the quantity and generic type of hydrocarbons present in the samples and the amount of hydrocarbons and compounds containing oxygen that are produced during the thermal cracking of the insoluble organic matter. Following the pyrolysis stage, the residual organic material is sent to a second oven (heating is between 350°C and 850°C) to determine its total organic carbon content (TOC) by oxidation under air (Lafargue et al. 1998). Lafargue also reported that the application of this instrument could be expanded to include the evaluation of oil-contaminated sites by making it possible to start the analysis at a low temperature (100°C) and by adjusting the heating rates in order to release different petroleum cuts such as gasoline, diesel, heavy oils, and lubricant oils, etc. However, Lafargue stated that "Rock-Eval-6 data can be correlated to standard environmental data such as infrared response. They are also complementary to infrared or

gas chromatographic analysis because they allow rapid screening of a large number of samples, thus helping to identify the samples that are worthy of additional study". He also reported the results of two studies where this instrument was used to identify the type of spilled hydrocarbon, i.e., diesel, etc. This report was the only one found in the literature on the use of this instrument in the environmental field.

This is the first application of this instrument for monitoring oily sludge biodegradation (the reported two studies were used to identify the types of hydrocarbon contaminant by characterizing hydrocarbon components using the pyrolytic parameters of Light Volatile Hydrocarbons (LV), Thermally Distilled Hydrocarbons (TD), and Thermally Cracked Hydrocarbons (TC)). For a description of the method, see Appendix A.

The collected samples from the cells were analyzed by the Rock-Eval-6. The raw data from the instrument provided the values of LV, TD, and TC. These values were plotted against time to show the trend in hydrocarbon concentrations (Figures 4.8, 4.10, and 4.11, respectively).

4.4.1 Light Volatile Hydrocarbons (LV)

The light volatile (LV) data correspond to the hydrocarbon compounds that are volatilized at or below 210°C. These compounds include aliphatics (up to C_{20}), aromatics with low molecular weight, and some resins. Each sample was analyzed twice and the arithmetical mean of both results are listed in Table 4.9. The data were also plotted against time (similar to the O&G plots). Figure 4.8a is the mean for LV concentration for

all landfarm cells and Figure 4.8b is the mean for LV concentration for the three-bioreactor cells. Even though there is some variability in these data, a trend similar to that of the O&G data can be observed where a noticeable drop in the LV levels started from day 171. The variability in the results may be attributed to the number of samples analyzed being small (2 samples), the size of the analyzed samples (100 mg), and the homogeneity of the samples. The initial and final levels of LV for every cell were plotted as bar graphs (Figure 4.9). The first bar (for each cell) represents the average of the first three data sets collected in September, October, and November 2000, and the second bar represents the average of the last three data sets collected in July, August, and September 2001.

The percentage of total LV loss for each cell is shown in Figure 4.9. The maximum decrease was at LF5 (64%) followed by BR3 (59%), while the lowest decrease (17%) was at LF4. Since the LVs include aliphatics, aromatics, and some resins, these drops are attributed to biodegradation as well as weathering (Section 4.3.1). The total decrease of LV in LF4 was low (17%). This value was calculated based on the average of the first three data sets and the last three data sets. When the data were evaluated, it was noticed that the reported concentration for the month of August was higher than that observed in July and September. As a result, a second attempt to recalculate the total loss for all cells was conducted. The total loss was calculated based on the basis of the average of the first two data and the last two data (instead of three data). The difference in the total LV loss between the two calculations ranged from 2 to 5%. The only exception was LF4 where the difference between both attempts was 10% (the total loss in the first attempt was

17%; in the second, 7%). It was decided to use the results of the first attempt because the difference for all nine cells (except LF4) was not significant and in order to have the same basis (average of three data) when comparing the LV and O&G results.

Table 4.9 Mean Light Volatiles Hydrocarbons (LV)-(mg/Kg) for all cells

Date	LF1	LF2	LF3	LF4	LF5	LF8	BR2	BR3	BR4
9/26/2000	13343	9625	10188	7795	14213	20465	8415	11345	14468
10/24/2000	14460	11320	11880	5845	8580	13963	7128	9395	10765
11/26/2000	14310	11625	10325	8690	6975	13640	8250	7960	11455
12/17/2000	15250	8625	7000	7205	6660	15990	7970	8260	10190
1/9/2001	15990	10065	11075	5795	10340	18685	8560	8525	12880
2/3/2001	15970	8570	9990	5585	5675	17145	5615	6082	11180
3/11/2001	14240	8765	12140	6400	7945	15335	8170	7220	10995
4/9/2001	8450	4180	7445	3200	3280	11180	5005	5795	7895
5/7/2001	12665	6385	5965	3590	3505	10680	4270	4740	7085
6/2/2001	10870	3870	6160	3100	3345	12565	4725	4815	9700
7/8/2001	10730	5430	6920	5690	3070	8220	3810	4260	7600
8/5/2001	10400	6700	6540	6980	3950	9120	4660	3630	8020
9/4/2001	8290	4735	5420	5765	3555	9010	3440	3755	7700

It is interesting that LF4 shows the lowest decrease in both the O&G and LV results conducted by the two different methods. The LV results for LF4 again stresses that the nutrients in LF4, without the addition of water, caused the soil to become more compacted and acted as a cover, which minimized the evaporation effect. The LV reduction in LF5 and BR3 (both had the same treatment) was close (64% and 59%, respectively) and the LV reductions in the cells that were left under natural attenuation treatment (LF1 and BR4) were also close (30% and 36%).

The similarity in the LV drop between cells that had similar treatment indicated that the LV results are compatible. The low decrease in LV for cells LF1 and BR4 is mainly due to the absence of watering, nutrients and tilling. The reason that BR4 had a greater

decrease in its LV levels than LF1 is probably due to the cover maintaining a higher temperature inside the cell. The LV reduction in LF2, LF3, LF8 and BR2 was also close (48%, 42%, 45%, and 50%), although these cells had different treatments. Since all cells show a decrease in their LV levels and since the GC/FID results showed that only a few cells had significant n-alkane reduction, it can also be concluded that the reduction in the LV levels is due to both weathering and in a few cases, biodegradation.

One of the characteristics of the LV output is to measure the hydrocarbons with low molecular weight (aliphatics and aromatics). Since the LV and the O&G reductions follow the same trend, it can be concluded that the LV output from the Open System Pyrolysis is an effective method for monitoring the degradation of low molecular weight hydrocarbon compounds.

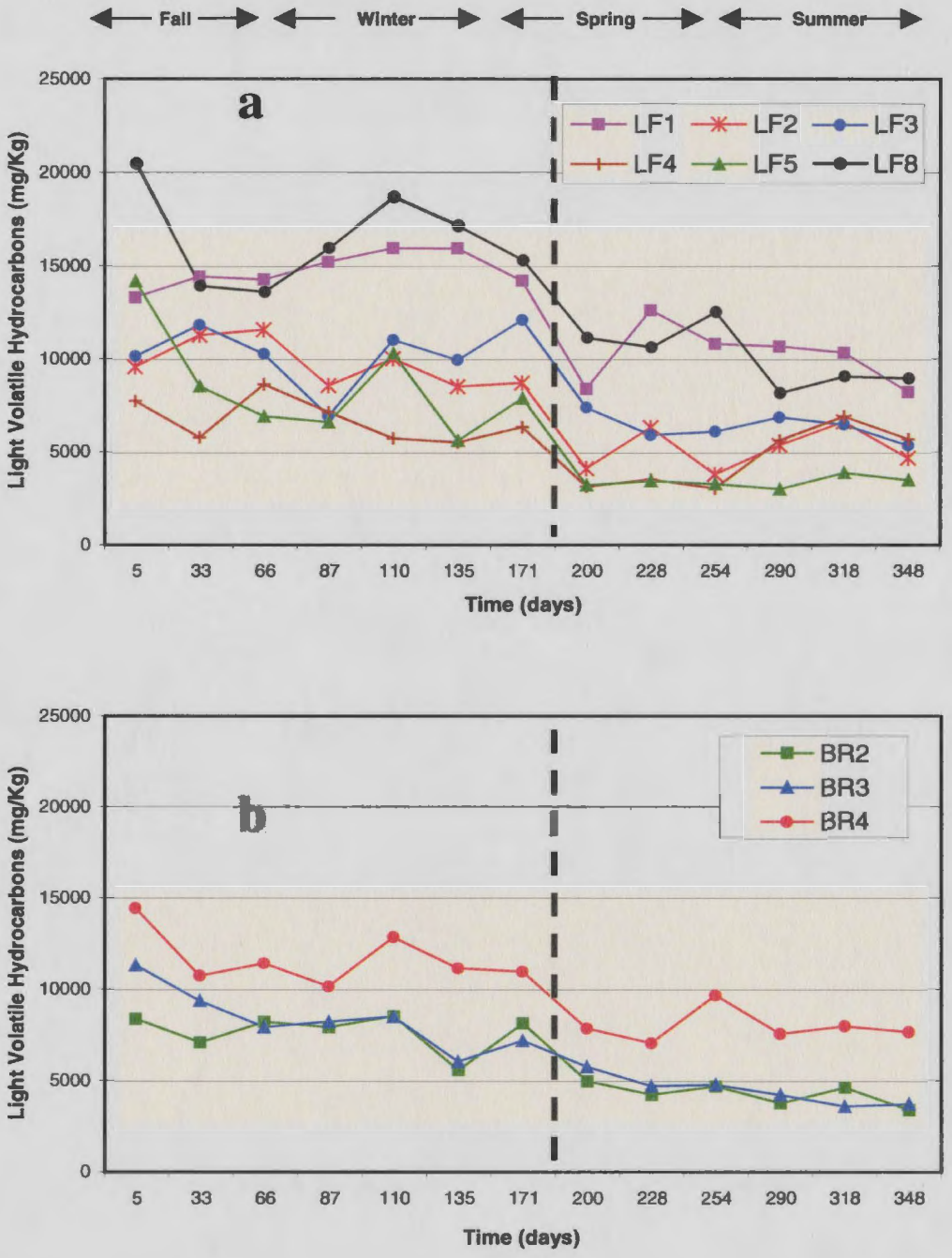

Figure 4.8 Mean LV concentrations versus time: (a) landfarm and (b) bioreactor cells

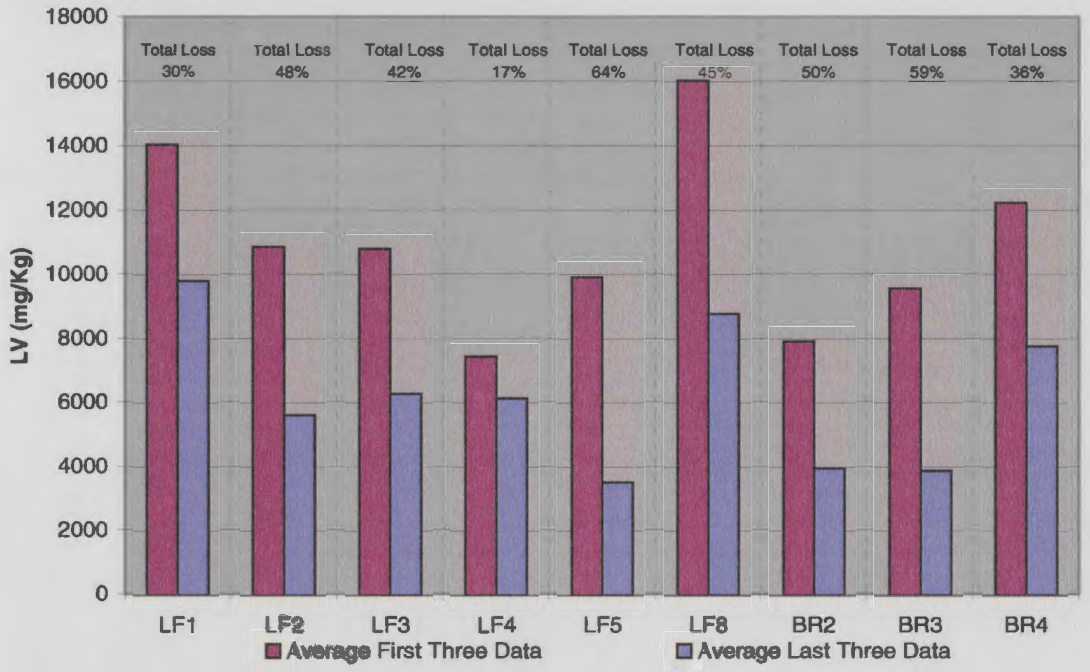

Figure 4.9 Bar graphs showing the initial and final LV levels for all cells

4.4.2 Thermally Distilled Hydrocarbons (TD)

The thermally distillable (TD) data corresponded to the hydrocarbon compounds that are thermally desorbed between 210°C and 400°C. These compounds include aliphatics (C20+), most of the aromatics, most of the resins, and some asphaltenes. Each sample was analyzed twice and the arithmetical mean of both results are listed in Table 4.10. The data were also plotted against time (similar to the O&G plotting). Figure 4.10a is the mean TD concentration for all landfarm cells and Figure 4.10b is the mean TD concentration for the three bioreactor cells.

Table 4.10 Mean Thermally Distilled Hydrocarbons (TD)-(mg/kg) for all cells

Date	LF1	LF2	LF3	LF4	LF5	LF8	BR2	BR3	BR4
9/26/2000	14653	10568	11550	9078	14435	30510	8668	12850	19970
10/24/2000	17040	13765	18188	8288	12635	26395	10833	15328	12893
11/26/2000	21955	14300	11710	18145	10800	24440	10980	11895	12400
12/17/2000	21580	9280	8395	11800	12730	31255	14205	13245	11965
1/9/2001	18970	10600	13835	10605	19065	31350	10070	11805	12600
2/3/2001	17610	8250	11290	8520	8550	32920	8280	7620	10890
3/11/2001	14850	9280	13420	10065	13705	28745	11855	9250	10810
4/9/2001	12688	6602	14055	8583	8716	34532	10610	11658	11161
5/7/2001	24191	12126	9998	8600	9263	29672	9199	9992	10491
6/2/2001	16662	4875	9819	6658	8232	26743	10077	10784	15683
7/8/2001	19008	9424	12851	18235	7954	26323	9497	10489	10961
8/5/2001	21235	11673	10475	18773	11135	27396	11998	8881	13201
9/4/2001	21023	8296	12130	13388	9475	30016	8393	9073	12721

The TD data showed more variability than the LV data. Degradation was not apparent and the trend for each cell is almost a straight line. Some of the cells (LF1, LF3, and LF4) showed an increase in their TD level after one year compared to their initial concentrations, while other cells (LF5, BR2) hardly showed any changes (Table 4.10). Since the TD data did not show any significant sign of reduction in the hydrocarbons, it can be concluded that the TD output is a good indicator for the presence of hydrocarbons that have low biodegradability. Shailubhai referred to this phenomena as 'sparing', where the microorganism with a broad substrate range is offered more than one type of organic substrate, it will not attack the substrates simultaneously but in a definitive sequence where it will start attacking the lowest molecular weight group, such as the n-alkanes, and only after this group is completely biodegraded, it will move into the next higher molecular group and this process will continue for other groups. It is also expected that if the study continued for a longer period (1-2 more years), the TD data would show reductions in their levels as a result of the degradation of the high molecular weight hydrocarbons. Raymond et al. (1976) and Huddleston and Meyers (1979) reported that

maximum petroleum hydrocarbon reductions of 35-79% could be obtained between nine months and nine years. Salanitro (2001) stated that a reduction from 35-89% was achieved in landfarms between one to 2.5 years. Therefore, it can be concluded that the TD output generated from the Rock-Eval-6 can be an effective indicator for monitoring of the presence and eventually the degradation high molecular weight hydrocarbons.

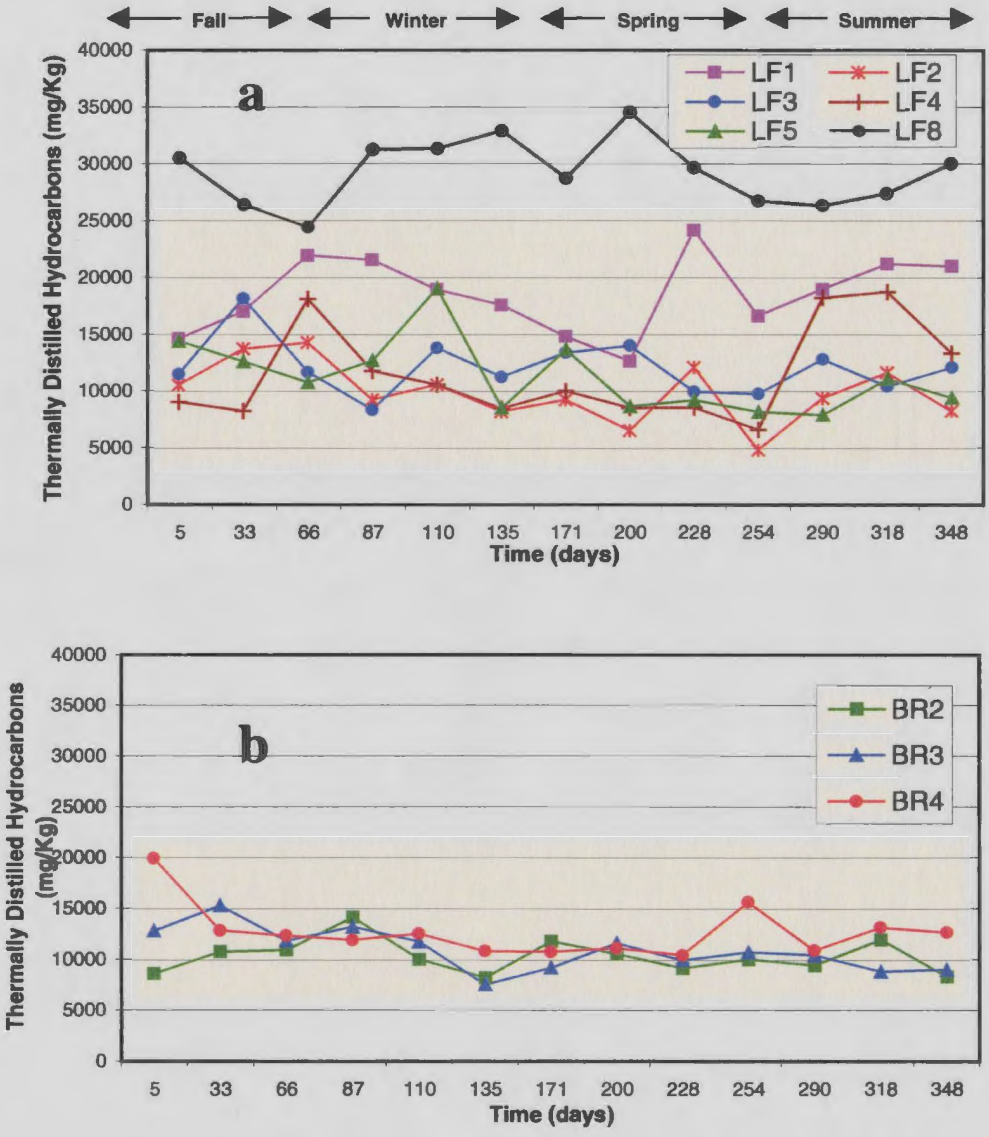

Figure 4.10 Mean TD concentrations versus time: (a) landfarm and (b) bioreactor cells

4.4.3 Thermally Cracked Hydrocarbons (TC)

The thermally crackable (TC) data corresponded to the hydrocarbon compounds that cracked at temperatures between 400°C and about 630°C. This represents the major asphaltene group plus some resins. Each sample was analyzed twice and the arithmetical mean of both results are listed in Table 4.11. Figure 4.11a is the mean TC concentration for all landfarm cells and Figure 4.11b is the mean TC concentration for the three bioreactor cells.

Table 4.11 Mean Thermally Cracked Hydrocarbons (TC)-(mg/kg) for all cells

Date	LF1	LF2	LF3	LF4	LF5	LF8	BR2	BR3	BR4
9/26/2000	10220	7258	8945	7223	11040	25095	6633	9733	13858
10/24/2000	11138	9903	14010	6785	10530	22715	8938	11475	9718
11/26/2000	15320	10865	9750	15835	9580	21570	9545	10095	10100
12/17/2000	14360	7745	6310	10800	11330	26060	12740	11445	9690
1/9/2001	13550	8610	10645	9770	16175	27075	9030	10465	9745
2/3/2001	13400	6820	9190	8160	7870	28170	7670	6660	9280
3/11/2001	10405	7225	10900	9565	12725	23040	10460	8000	8795
4/9/2001	7702	4293	9100	7367	8949	25683	8770	8692	7259
5/7/2001	15659	7944	6692	7825	8432	22828	7371	8588	7139
6/2/2001	10398	3135	6566	5557	7533	20777	8948	9991	10282
7/8/2001	13112	6146	8949	18285	10266	23367	9233	10161	7869
8/5/2001	14165	7957	7035	15317	11225	26904	11422	9589	9769
9/4/2001	14997	5624	9340	12287	13690	29169	9827	10267	9624

When evaluating the TC data it was noted that most of the cells did not show any definite trend in their TC concentrations. This can be attributed to: i) the small size of the sample used in the analysis (2 mg), and ii) TC data represents mainly the asphaltenes fraction and some resins, which are recalcitrant to biodegradation (Huesemann 1994). The trends in the TC data were similar to the TD data where both did not show any sign of degradation as supported by a general straight-line trend in the results. From this it can be concluded

that TC output generated from the Rock-Eval-6 can be an effective indicator for monitoring the presence of recalcitrant hydrocarbons.

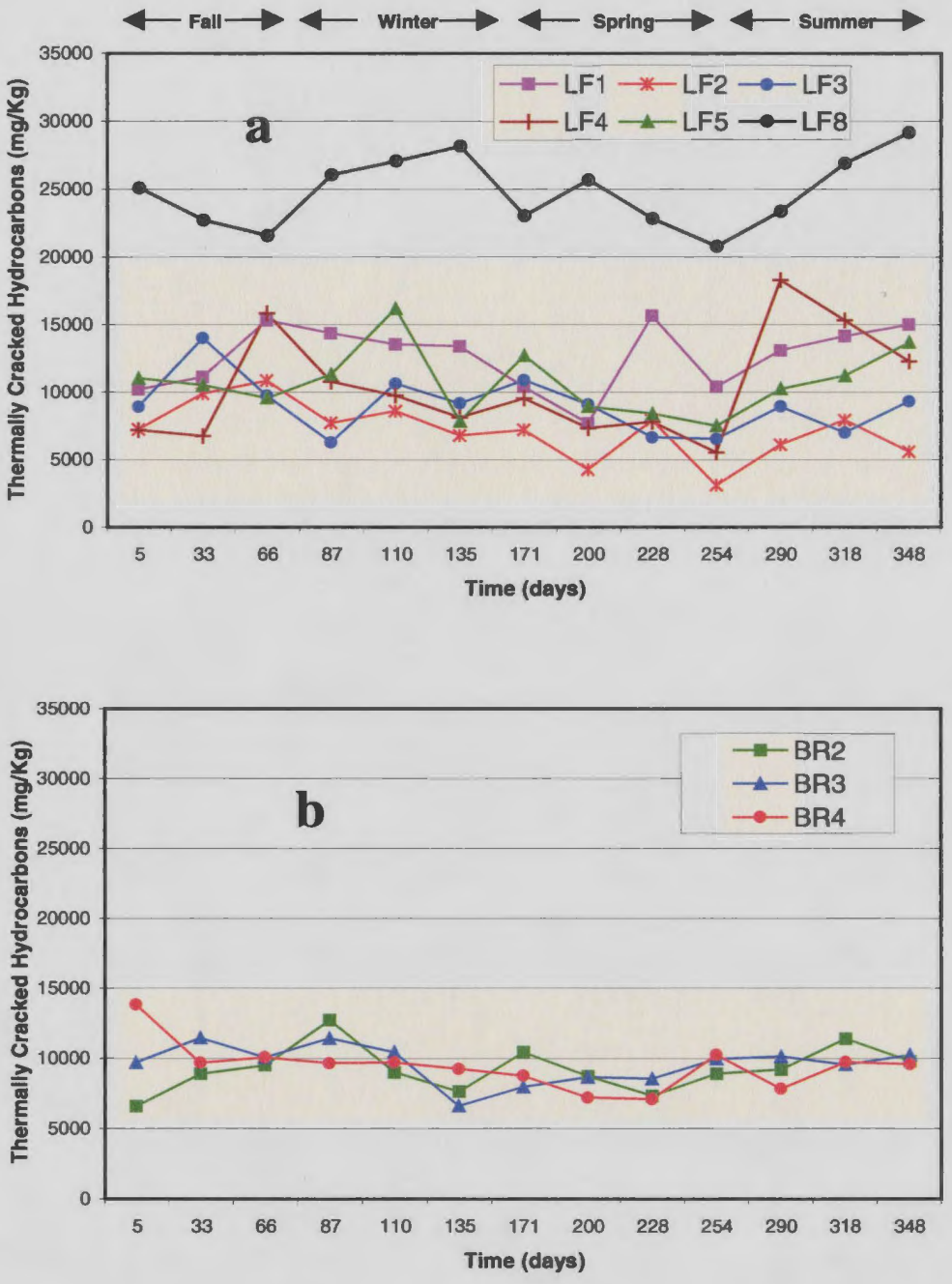

Figure 4.11 Mean TC concentrations versus time: (a) landfarm and (b) bioreactor cells

4.4.4 Total Hydrocarbons (TH)

Total Hydrocarbon is equivalent to the sum of the Light Volatile (LV), Thermally Distilled (TD), and Thermally Cracked (TC) Hydrocarbons. The TH results are listed in Table 4.12 and are also plotted against time in Figures 4.12a and 4.12b. The TH results do not show a clear decreasing trend because two of its three components (TD and TC) did not show any significant changes in their measured concentrations. Had the study been continued to allow for the degradation of high molecular weight compounds, it is believed that the TH results would have shown a clear trend reflecting the decrease in the concentrations of its three components. Therefore, it can be concluded that the TH output can be used as an indicator for monitoring a gross quantity of hydrocarbons in the soil.

Table 4.12 Total Hydrocarbons (TH)-(mg/kg) for all cells

Date	LF1	LF2	LF3	LF4	LF5	LF8	BR2	BR3	BR4
9/26/2000	38215	27450	30683	24095	39688	76070	23715	33928	48295
10/24/2000	42638	34988	44078	20918	31745	63073	26898	36198	33375
11/26/2000	51585	36790	31785	42670	27355	70360	28775	29950	33955
12/17/2000	51190	25650	21705	29805	30720	73305	34915	32950	31845
1/9/2001	48510	29275	35555	26170	45580	77110	27660	30795	35225
2/3/2001	46980	23625	30470	22265	22095	78235	21570	20362	31345
3/11/2001	39495	25270	36460	26030	34375	67120	30485	24470	30600
4/9/2001	28840	15075	30600	19150	20945	71395	24385	26145	26315
5/7/2001	52515	26455	22655	20015	21200	63180	20840	23320	24715
6/2/2001	37930	11880	22545	15315	19110	60085	23750	25590	35665
7/8/2001	42850	21000	28720	42210	21290	57910	22540	24910	26430
8/5/2001	45800	26330	24050	41070	26310	63420	28080	22100	30990
9/4/2001	44310	18655	26890	31440	26720	68195	21660	23095	30045

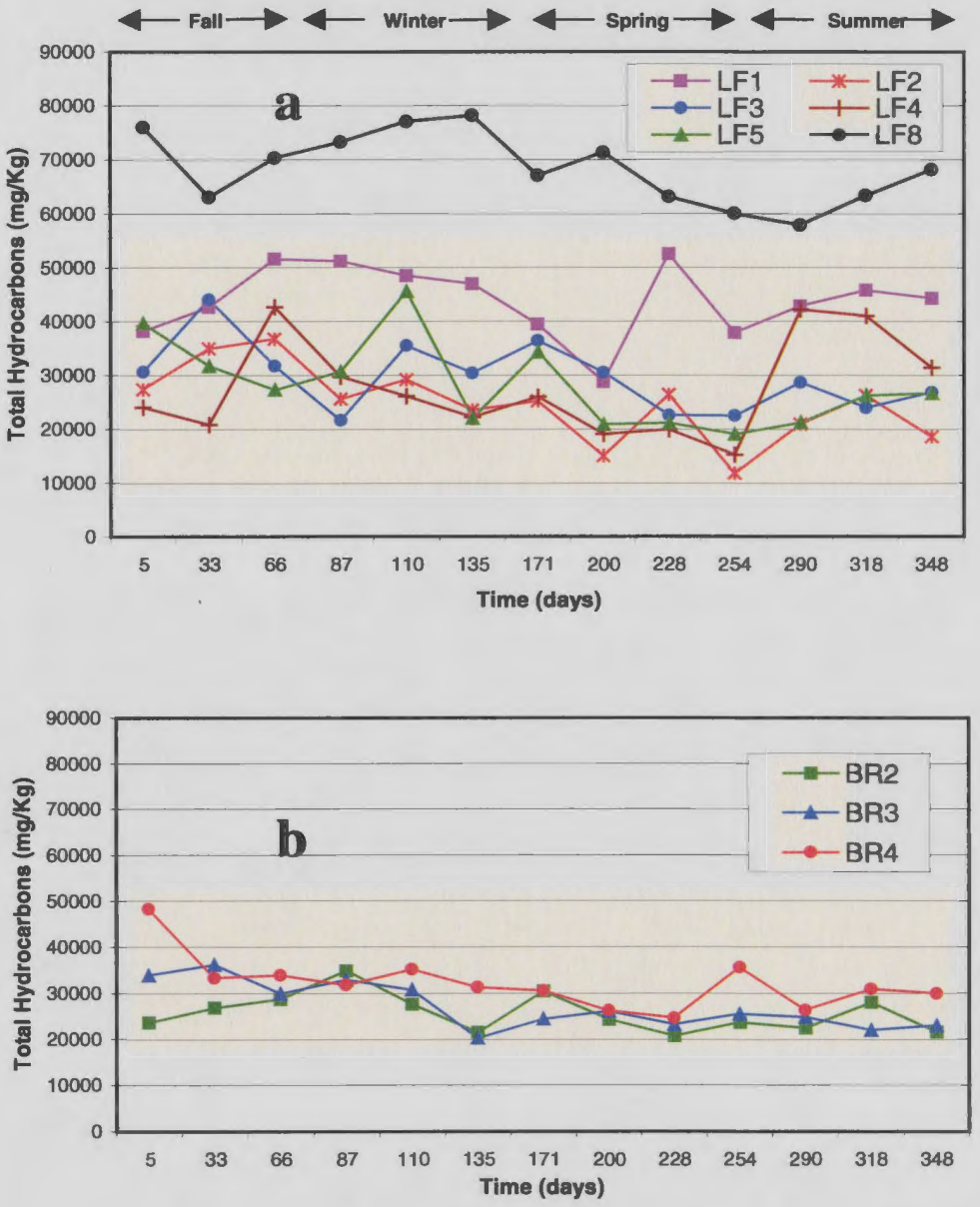

Figure 4.12 Mean TH concentrations versus time: (a) landfarm and (b) bioreactor cells

The initial and final TH levels as well as the total TH loss for each cell were plotted as bar graphs (Figure 4.13).

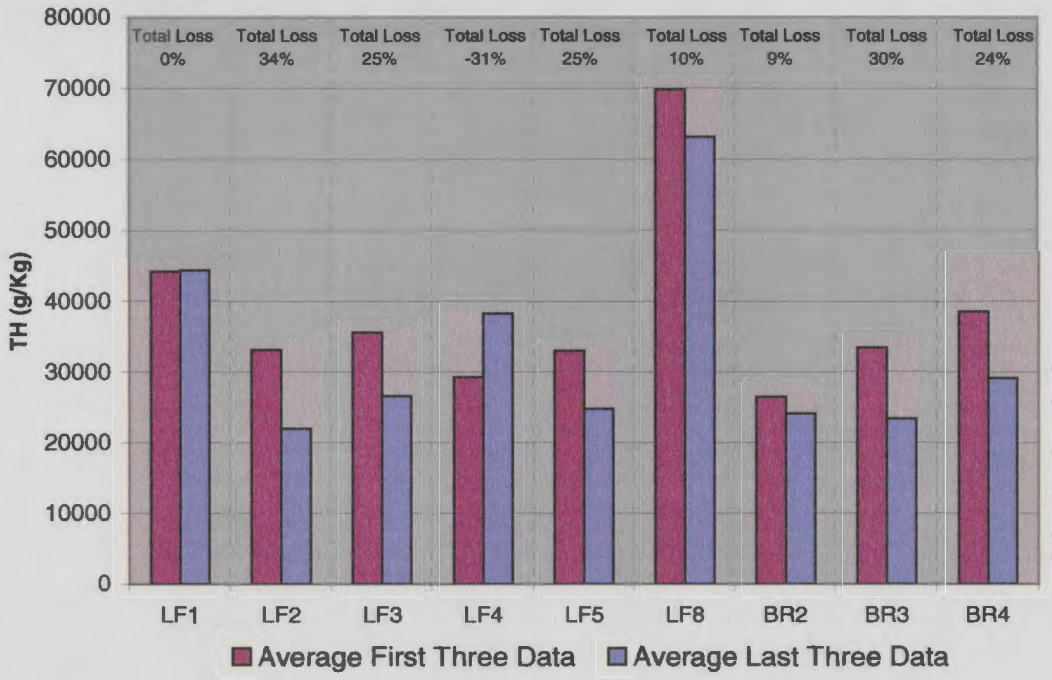

Figure 4.13 Bar graphs showing the initial and final TH levels for all cells

4.5 Comparison Between O&G and Open System Pyrolysis

In order to draw a definitive conclusion about the similarity of the Open System Pyrolysis method and the typical O&G method, a comparison between the results obtained from this study for both methods was conducted. However, this comparison was done in two parts: the first compared the O&G and the TH results: the second compared the O&G and the LV results. The latter was conclusive since a similar trend was observed between the results of both methods.

4.5.1 O&G Versus TH

The TH results of the Open System Pyrolysis (Table 4.12) were compared to the O&G results (Table 4.2) in order to determine if any relationship existed between these two

methods. When the measured concentrations from both tables were compared to each other, it was clear that O&G concentrations were two to three times higher than their TH counterparts and, as a result, no relationship could be determined between the data from both methods. It was then decided to compare the percentage reduction for O&G with that of TH in order to see if any similarity existed in the degradation trend. Figure 4.14 shows the percentage reduction for O&G and TH for each cell.

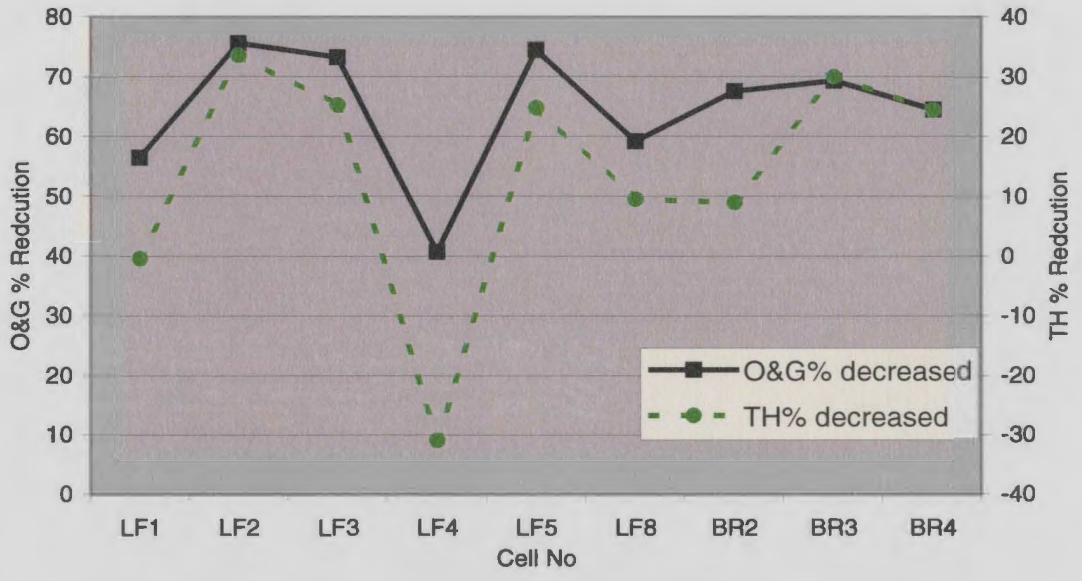

Figure 4.14 Percentage reduction for TH and O&G

When evaluating the observed information from the TH and O&G bar graphs (Figures 4.13 and 4.4) and from Figure 4.14, the following similarities were noted:

- The percentage reductions in both methods follow the same trend.
- The highest percentage of total loss in both methods was measured at LF2 (76% for O&G and 34% for TH).
- The lowest percentage of total loss in the O&G method was measured at LF4 (40%); however, for the TH method, LF4 showed an increase of about 31%

instead of a decrease. Even though the increase in the final TH concentrations in LF4 is questionable, this cell is still considered to have the lowest total loss.

- LF1 shows the second lowest percentage of total loss in both methods (57% for O&G and 0% for TH).
- The percentage of total loss in LF3, LF5, BR3 and BR4 were close to each other in both methods.
- BR2 is the only cell that did not show any similarity in both methods. The total loss in the TH levels for BR2 (9%) is low compared to BR3 (30%) and BR4 (24%). It is believed that analytical errors are the cause of this low level.

From the above it can be concluded that both methods appear to have some similarities, but more work is needed in order to draw a definite conclusion.

For the first two months of the study (September and October 2000), both O&G and TPH analysis was conducted for all collected samples. The TPH analyses were later discontinued due to the time consuming process and the amount of solvent required. Since the O&G and TH values were different, it was decided to include the measured TPH values in this comparison. Table 4.13 shows the measured concentrations of TPH, TH and O&G for September 26 and October 24, 2000. From this table, a clear similarity between the measured values of TPH and TH was observed. However, since the TH values include LV, TD, and TC and since TC covers the asphaltenes and resin compounds and, on the other hand, the TPH values do not include the polar compound, the concern whether these two methods represent the same groups of hydrocarbon was

raised. In order to clarify this concern, further analytical work is required. However, one theory that can explain this similarity is that the heavy molecular weight compounds (asphaltene and resins) went through the cooking at the second stage of the pyrolysis, which led to these compounds not being detected by the TH. This also explains why the TC results did not change during this test. However, more in-depth investigation is required to verify this hypothesis.

Table 4.13 Comparison of TPH, TH, and O&G- (mg/kg)

Cell number	9/26/2000			10/24/2000		
	TPH	TH	O&G	TPH	TH	O&G
LF1	37575	38215	134747	23830	42638	110313
LF2	28664	27450	103978	28941	34988	104480
LF3	35266	30683	102775	35684	44078	114467
LF4	18807	24095	85280	19734	20918	49307
LF5	35412	39688	102373	19873	31745	117380
LF8	82722	76070	181770	53411	63073	156143
BR2	39982	23715	87040	18803	26898	75597
BR3	35994	33928	89628	18920	36198	75450
BR4	29469	48295	91775	20235	33375	87690

Table 4.14 shows a comparison between the TH and the O&G methods. In this table, eight criteria were compared. The results clearly show that the TH method is more cost effective than the O&G method.

Table 4.14 Comparison between TH and O&G methods

Criteria	Method	
	TH	O&G
Principle of the used method	volatilization (temp.)	solvent extraction
Applicability of the method	all hydrocarbons	all hydrocarbons
Time required for the analysis of each sample	30 minutes	8 hours
Use of solvents	No	Yes (the use of solvent has adverse environmental Impact)
Characteristics of method	simple	simple
Size of sample used	100mg*	10g
Cost of operation	low	High

* One disadvantage of the TH method is the size of the sample to be analyzed (only 0.1 gram sample) is much smaller than that used for O&G method (10 gram sample), which may increase sampling errors. To overcome this problem, more samples should be analyzed. Alternatively, a larger sample (e.g. 2 gram) should be homogenized prior to analysis.

Huesemann (1994), Shailubhai (1986), and Morgan et al. (1989) listed various hydrocarbon groups according to their susceptibility to degradation in the following order: mono-aromatics > straight-chain alkanes > branched alkanes > saturated cyclic > PNA > polars. The O&G method does not give any definitive information on the above hydrocarbon groups based on their susceptibility to degradation, but rather gives a single number. On the other hand, the Open System Pyrolysis method gives more details on the specific hydrocarbon groups that have been degraded. Even though these groups are not exactly in line with the groups reported by the literature in terms of their susceptibility to degradation, they still give a better indication of what groups have degraded and the degree of their degradation. More studies would better relate the Rock-Eval-6 data against the order of degradation reported by the literature.

In conclusion, the results of this study show that the pyrolysis method has great potential to be used for monitoring the degradation of hydrocarbons. This method also has

advantages over the typical O&G method in that it can identify the hydrocarbon groups on the basis of their potential degradation and it can provide more representative results.

4.6 Performance Evaluation of Individual Cells

The following is a discussion of the performance for each of the landfarm and bioreactor cells.

4.6.1 LF1 (No Action)

The intent of cell LF1, which was designated as the control cell, was to study the kinetics of oily sludge degradation in a landfarm under natural attenuation conditions.

Remediation by natural attenuation has started to receive more attention in the last few years as an option for remediating contaminated sites (Swett 1998; Nyer et al. 1998; Buchanan et al. 1999; O'Steen 1999; Odermatt 1999; Khan and Husain, 2001). However, there were no published studies related to the applicability of this method as a treatment method for oily sludge. As a result, it was decided to test the applicability of this method, under arid conditions, by designating cell (LF1) for monitoring the hydrocarbon degradation under natural conditions in order to determine the effectiveness of natural attenuation processes. Since most of the work done under natural conditions was mainly conducted in the US, it was more tempting to conduct this study in Saudi Arabia especially where the climate conditions (arid) are different than those in the US. The results from this cell will clarify the effectiveness of natural attenuation as a method for treating oily sludge. They will also be compared with those obtained from the other

landfarm cells, with the aim of relying on this method as a treatment method instead of landfarming, if proven feasible.

The process of natural attenuation includes several components (biodegradation, sorption, dispersion, chemical reaction, and volatilization) with biodegradation being regarded as the most important one (Swett 1998; US EPA 1999). For this study, no tilling was applied, and no nutrients or water were added to this cell, with the exception of 9.9 mm of rain that fell between November and December 2000.

During the study period, the range of moisture content in LF1 was between 9.7% and 3.0% (Table 4.4). The evaporation effect on this cell was minimized by the fact that tilling was not applied. This was evident when the lowest measured moisture content in LF1 (3%) was compared with the lowest measured moisture content in LF3 (1.8%), which was watered and tilled on a regular basis. As discussed in Section 4.3.5.1, the moisture content in LF1 was sufficient to support microbial activity. The observed level of microbial counts was in the range of 2.2E+06 to 2.2E+10 GAB/g (Table 4.6), which is above the level required to perform the biodegradation process (Arora et al. 1982; Morgan et al. 1989).

The total reduction in the O&G concentration in LF1 during this study was approximately 57% (Figure 4.15 and Table 4.2). An initial drop in the concentration from 134,747 to 110,313 ppm occurred between days 5 and 33, and is believed to be due to heterogeneity in the initial sampling. Between days 33 and 135 the concentration

appeared to have leveled off in the range of 110.313 to 115.295 ppm, indicating that degradation was not taking place. Following this period, the O&G concentration declined significantly over the next 120 days, from 113.270 to 44.770 ppm, which coincided with the beginning of the summer season. This is believed to be mainly due to weathering during the hot season. The concentration again leveled off within the range of 44.770 and 57.480 ppm.

The ratios of C17/pristane and C18/phytane were plotted against time (Figure 4.16) to determine the extent of biodegradation. The ratios of C17/pristane and C18/phytane throughout this study decreased only slightly (the C17/pristane ratio was 3.59 in October 2000 and 2.95 in September 2001; the C18/phytane ratio was 2.2 in October 2000 and 1.95 in September 2001, Table 4.3) indicating that biodegradation was minimal. The gas chromatograph for the n-alkanes of LF1 (Figure 4.17) also showed that after one year there were small changes in the levels of n-alkanes. The only compounds that disappeared almost completely were the C10 and C11 n-alkanes; however, the volatilization rates for these compounds are greater than their microbial degradation rates (Salanitro 2001), which means that their disappearance is thought to be mainly due to volatilization, and the biodegradation effect is minimal under the climatic conditions prevailing in Saudi Arabia.

Summary

Despite the availability of microbes and water content, the degradation process in LF1 was mainly attributed to weathering. Biodegradation occurred but was minimal and can

be classified as light with a rank of 1 (Peters and Moldowan 1993). Since natural attenuation is known to be a long process (O'Steen 1999; Matson et al. 1999), it is believed that if the study had continued for a longer time, the effect of biodegradation would have been more apparent. However, from all of the findings, it is concluded that natural attenuation, which is an important process for remediating contaminated sites (Nyer et al. 1998), should not be used as an on-going treatment/disposal method for oily sludge, mainly because it takes a longer time to achieve the targeted treatment goals compared to enhanced treatment processes. On the other hand, this process should be used for remediating specific contaminated sites.

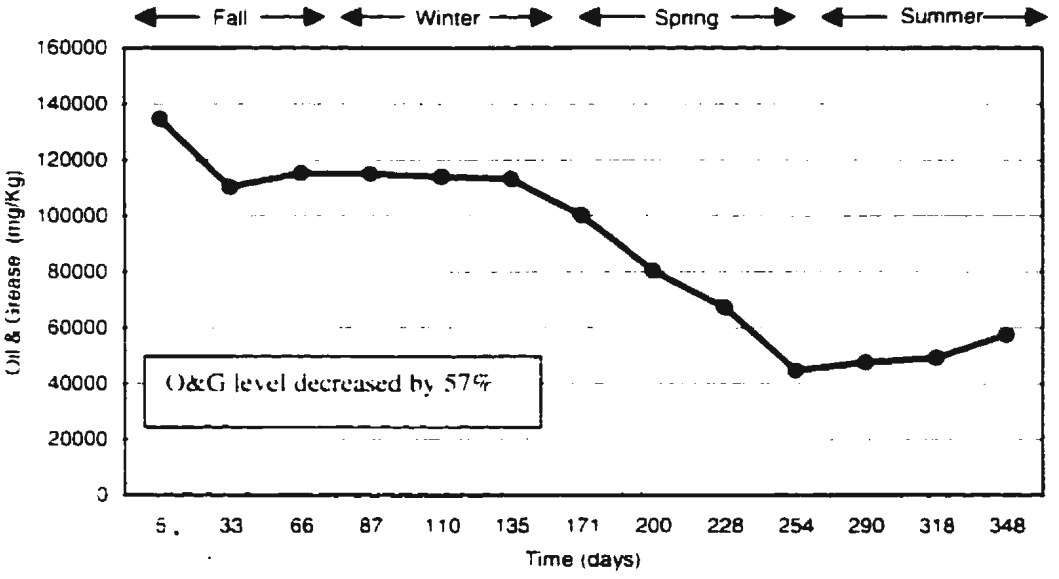

Figure 4.15 Oil & Grease concentrations versus time for LF1

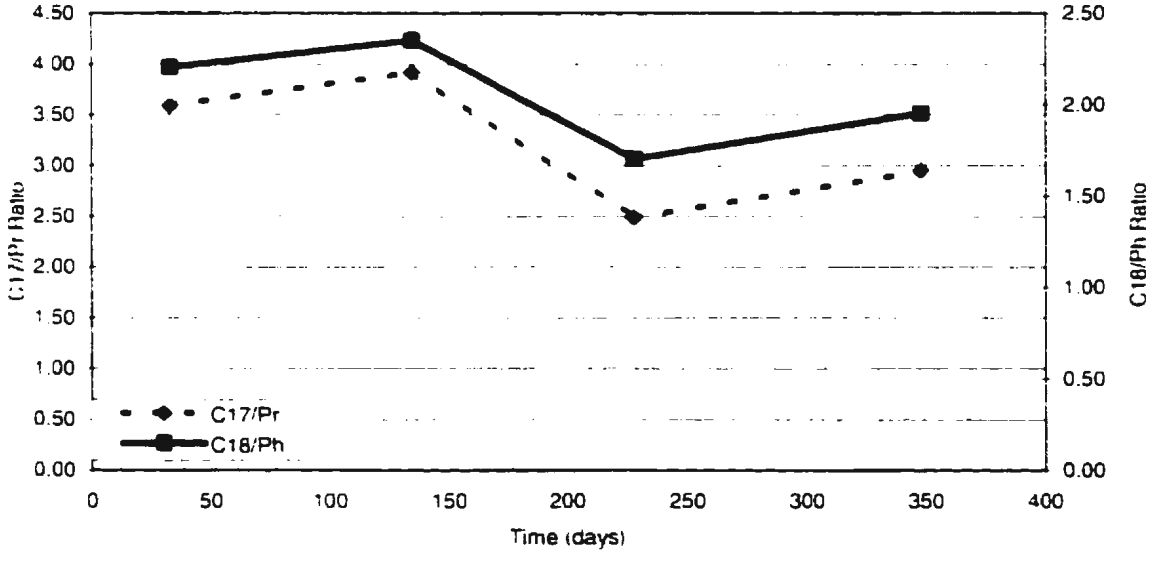

Figure 4.16 C_{17}/Pr and C_{18}/Ph ratios versus time for LF1

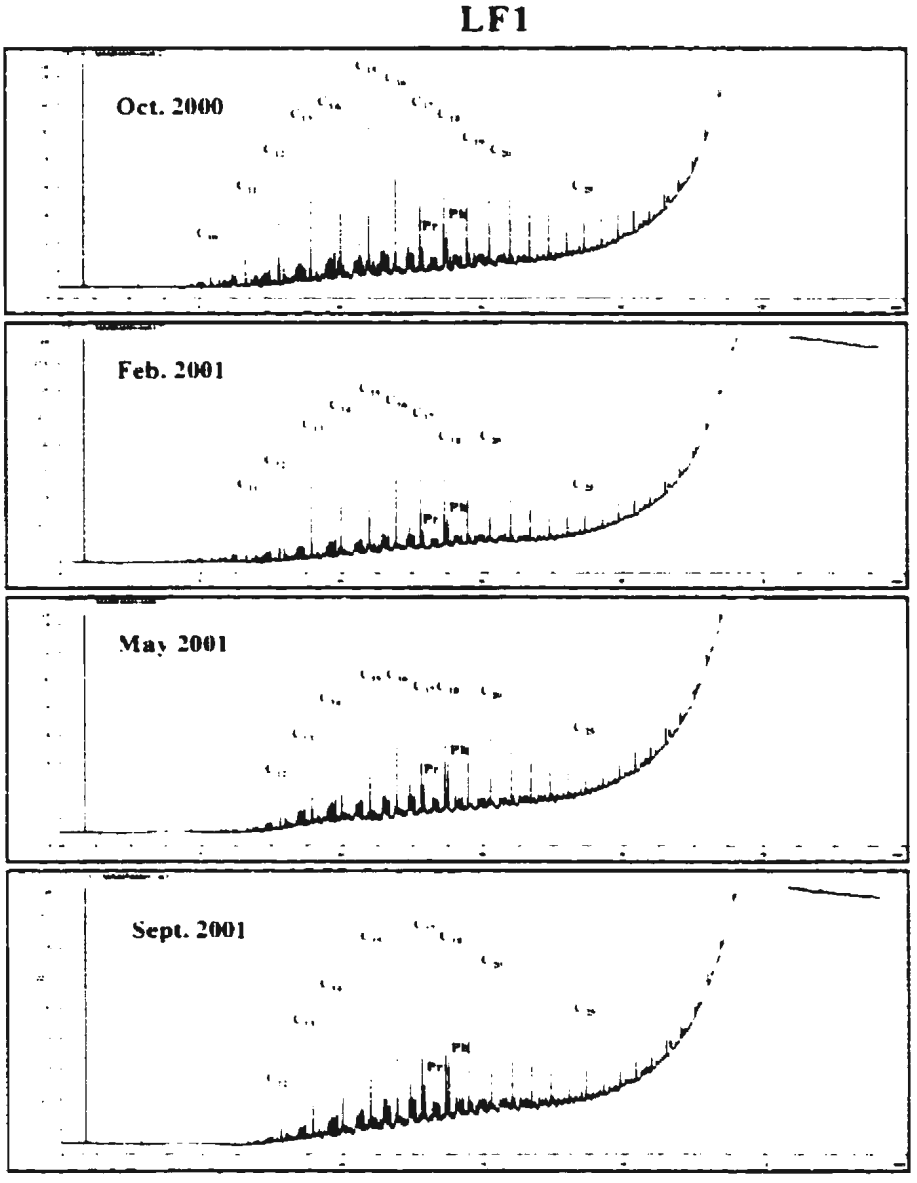

Figure 4.17 Gas chromatograph of LF1 sludge samples collected on Oct 2000, Feb 2001, May 2001 and Sep 2001

4.6.2 LF2 (Tilling)

The intent of LF2 was to study the kinetics of oily sludge degradation in a landfarm under enhanced conditions where only tilling was applied.

The moisture content range in LF2 during this study was between 7.3% and 1.3% (Table 4.4). When this range is compared with that of LF1 (both were not watered), it is clear that the moisture content in LF1 is higher than LF2. This is mainly due to the fact that LF2 was tilled on a regular basis; this increased the evaporation potential and led to less moisture in the cell. However, the moisture content in LF2 during the summer period was slightly below the range required to support microbial activity (Section 4.3.5.1). The observed level of microbial counts was in the range of 8.5E+04 to 2.3E+8 GAB/g (Table 4.6), which is slightly less than the microbial range in LF1 (2.2E+06 to 2.2E+10 GAB/g). This cell measured the lowest microbial counts among the cells. The lowest bacterial count (8.5E+04) was measured in June 2001, the month, which recorded the lowest moisture content (1.3%). The bacterial counts during the summer were below the required levels of 10^5 and 10^6 needed to perform the biodegradation process (Morgan et al. 1989; Arora et al. 1982). The low bacterial counts were mainly due to the low level of moisture in the soil and the hot temperature.

The total reduction in the O&G concentration in LF2 (76%) was the largest among all of the other nine cells (Figure 4.18). For the first 66 days, the concentrations appeared to have stayed constant without any significant changes. The decline in the O&G content started from day 66 (108,505 ppm) and continued until day 254 (13,643 ppm). Between

days 254 and 290, the concentrations increased from 13,643 to 24,207 ppm and then leveled off at a concentration of approximately 24,000 ppm for the remaining period of this study. Based on the trend of O&G decrease, the measured concentration in June (13,643 ppm) was uncharacteristically low. When comparing the degradation trend in LF2 with that in LF1, it was observed that the initial period, where no degradation occurred, was much shorter in LF2 and the period of degradation was longer. All of this is believed to be the result of tilling, which has enhanced the weathering process in LF2 and thus increased the rate of degradation.

The ratios of C17/pristane and C18/phytane were plotted against time (Figure 4.19) to determine the extent of biodegradation. There were hardly any changes in the ratios of C17/pristane and C18/phytane throughout this study (the C17/pristane ratio was 3.47 in October 2000 and 3.7 in September 2001; the C18/phytane ratio was 2.14 in October 2000 and 2.36 in September 2001, Table 4.3), indicating that biodegradation, if any was minimal. The gas chromatograph for the n-alkanes of LF2 (Figure 4.20) also showed that after one year a preferential weathering of light ends (C10, C11 and C12) occurred. Since the volatilization rates for these compounds are greater than their microbial degradation rates (Salanitro 2001), this indicates that the disappearance of these compounds was mainly due to volatilization and not biodegradation. In addition, it was noticeable that in the summer, the soil became very loose in consistency and during the sampling process the soil easily fell off the augers when they were extracted. Consequently, several soil auger extractions were needed to obtain reasonable amounts of representative samples from this cell.

Summary

From the above findings, it is concluded that weathering was the dominant degradation/hydrocarbon reduction process in LF2 and that biodegradation did not occur to any significant extent. It is proposed that the absence of fertilizers, as well as not adding water, made the soil very loose; this increased the weathering process and resulted in microbial counts being at a level lower than those needed to perform the biodegradation process. The extent of the biodegradation level can be classified as light with a rank between 2 and 3 (Peters and Moldowan 1993).

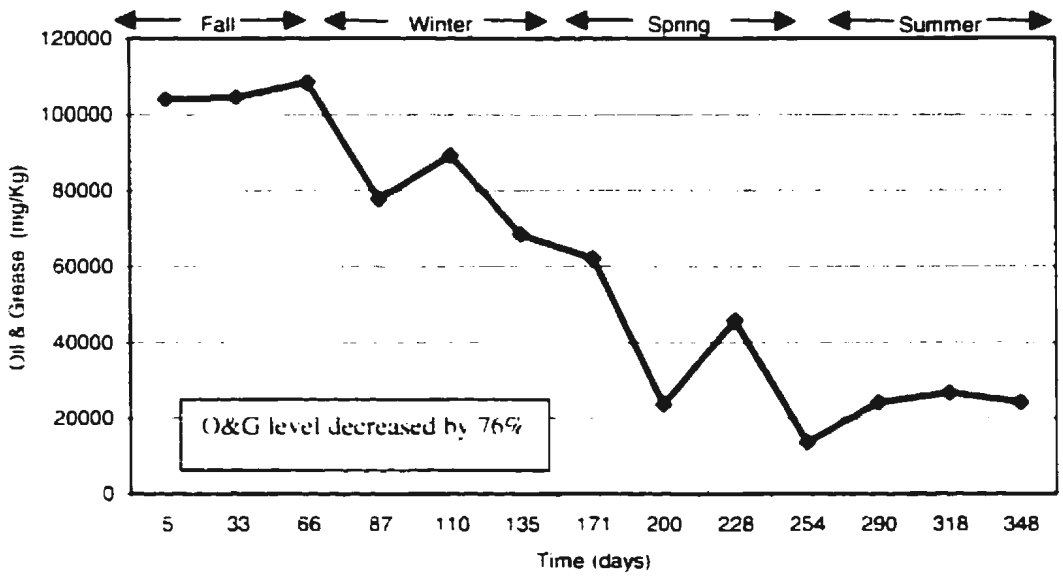

Figure 4.18 Oil & Grease concentrations versus time for LF2

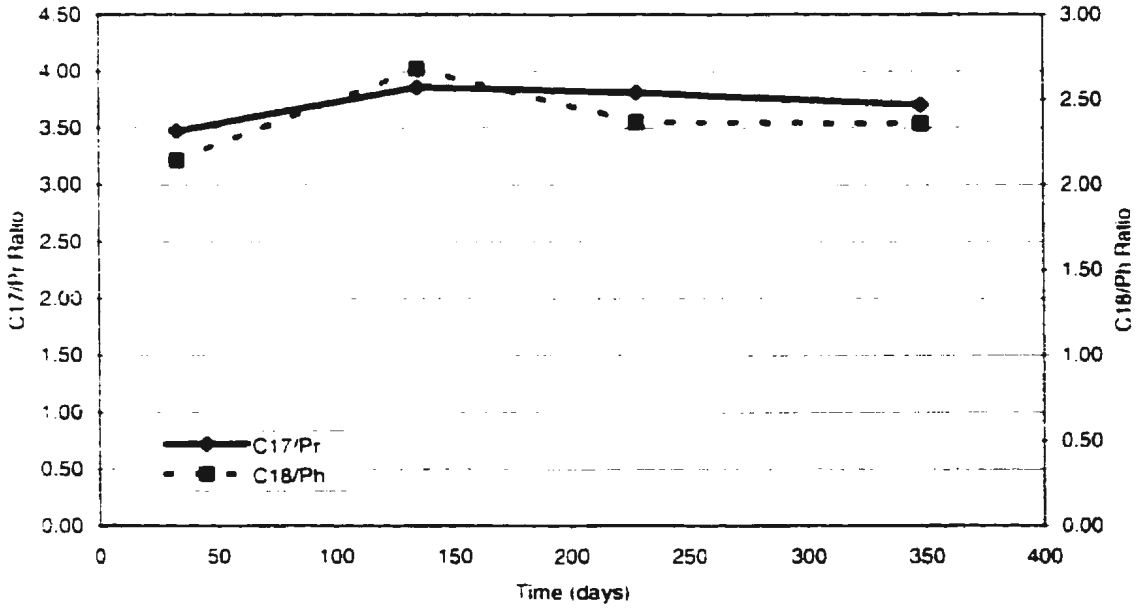

Figure 4.19 C_{17}/Pr and C_{18}/Ph ratios versus time for LF2

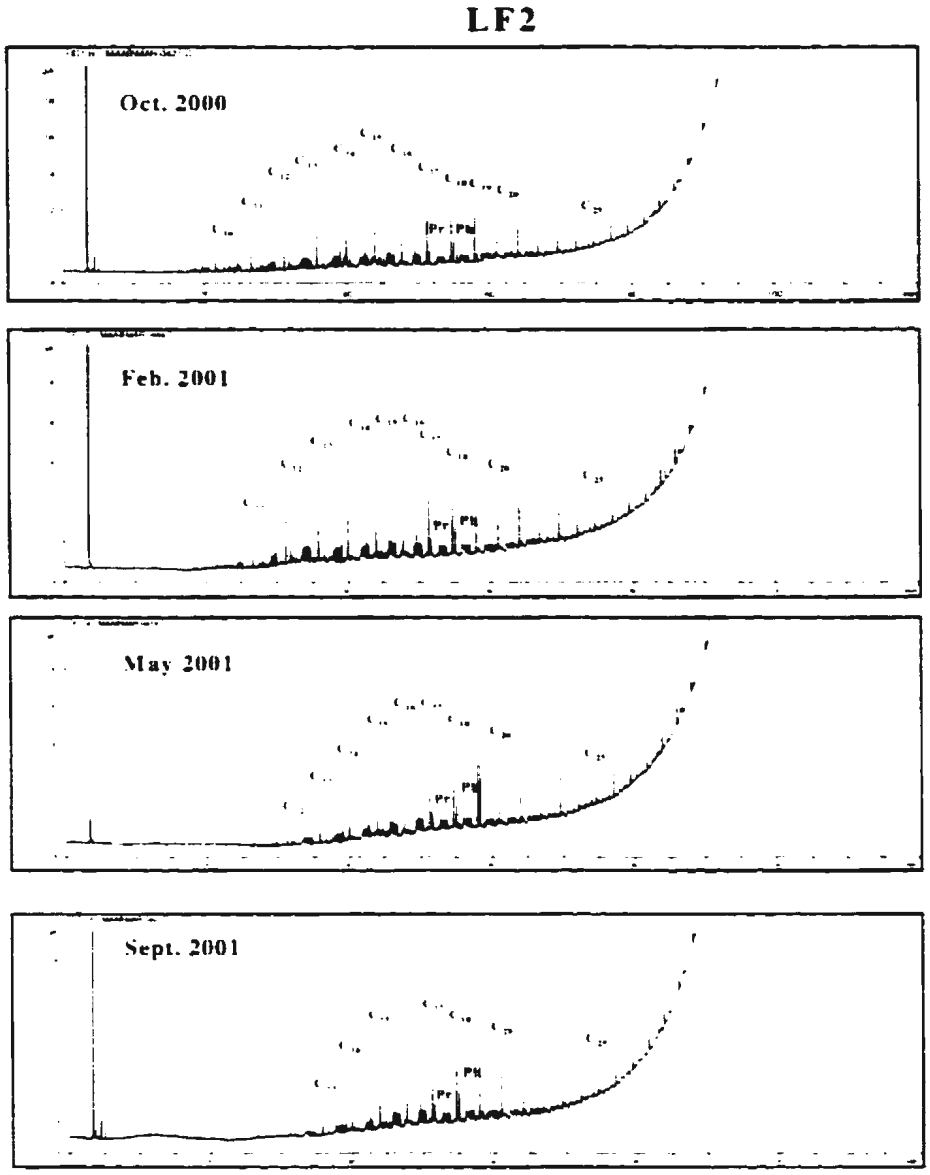

Figure 4.20 Gas chromatograph of LF2 sludge samples collected on Oct 2000, Feb 2001, May 2001 and Sep 2001

4.6.3 LF3 (Tilling + Water)

The intent of LF3 was to study the kinetics of oily sludge degradation in a landfarm under enhanced conditions where only tilling and water were applied.

The moisture content range in LF3 during this study was between 8.4% and 1.8% (Table 4.4). Even though LF3 was watered on a regular basis, the range of the moisture content in this cell was lower than in LF1. It is believed that this is mainly due to the high evaporation rate, which was enhanced by the tilling activities. The moisture content level dropped in June from 3.5% to 2.1% and stayed close to this level for the remaining time of the study. The observed level of microbial counts was in the range of 3.9E+05 to 9.1E+8 GAB/g (Table 4.6). The moisture level in LF3 was considered sufficient to support microbial activity (Section 4.3.5.1) and the microbial counts were above the level required to perform the biodegradation process (Arora et al. 1982; Morgan et al. 1989).

The total drop in O&G concentration in LF3 was approximately 71% (Figure 4.21). The concentrations between days 5 and 135 did not follow any consistent trend, but increased and decreased intermittently. However, from day 135 (end of winter) until day 254 (beginning of summer), O&G concentrations followed a consistent decreasing trend and decreased from 100,790 to 25,320 ppm. From day 254 until the end of the study, these concentrations maintained a steady state level that ranged from 33,680 to 26,860 ppm. Based on the trend of the O&G decrease, the measured concentration in December (67,060 ppm) was uncharacteristically low. When the degradation trend is compared with that in LF1, and the December value discarded, it is clear that the initial period where no

degradation occurred was similar to LF1. However, during the degradation period, the rate of degradation was much higher in LF3 than that in LF1. When the degradation trend of LF3 is compared with LF2 for the same period, it was observed that LF3 had less reduction in the O&G level (71%) than in LF2 (76%). From the discussion on LF2, it was shown that tilling was the main contributing factor for the decrease of the O&G level. It appears that adding water in LF3 might have slowed down the evaporation process, resulting in less decrease of O&G levels. However, to make a definite conclusion, more in-depth investigation is needed.

The ratios of C17/pristane and C18/phytane were plotted against time (Figure 4.22) to determine the extent of biodegradation. There was only a slight change in the C17/pristane and C18/phytane ratios throughout this study (the C17/pristane ratio was 3.81 in October 2000 and 3.18 in September 2001; the C18/phytane ratio was 1.98 in October 2000 and 2.29 in September 2001, Table 4.3), indicating that biodegradation was minimal. The gas chromatograph for the n-alkanes of LF3 (Figure 4.23) showed that after one year preferential weathering of light ends (C10, C11 and C12 n-alkanes) occurred. Since the volatilization rates for these compounds are greater than their microbial degradation rates (Salanitro 2001), this indicates that the disappearance of these compounds is mainly due to volatilization and that the biodegradation effect is minimal.

Summary

From all of these findings, it is concluded that weathering was the dominant degradation/hydrocarbon reduction process in LF3; however, biodegradation did occur to

a minor degree. The extent of the biodegradation level can be classified as light with a ranking between 1 and 2 (Peters and Moldowan 1993).

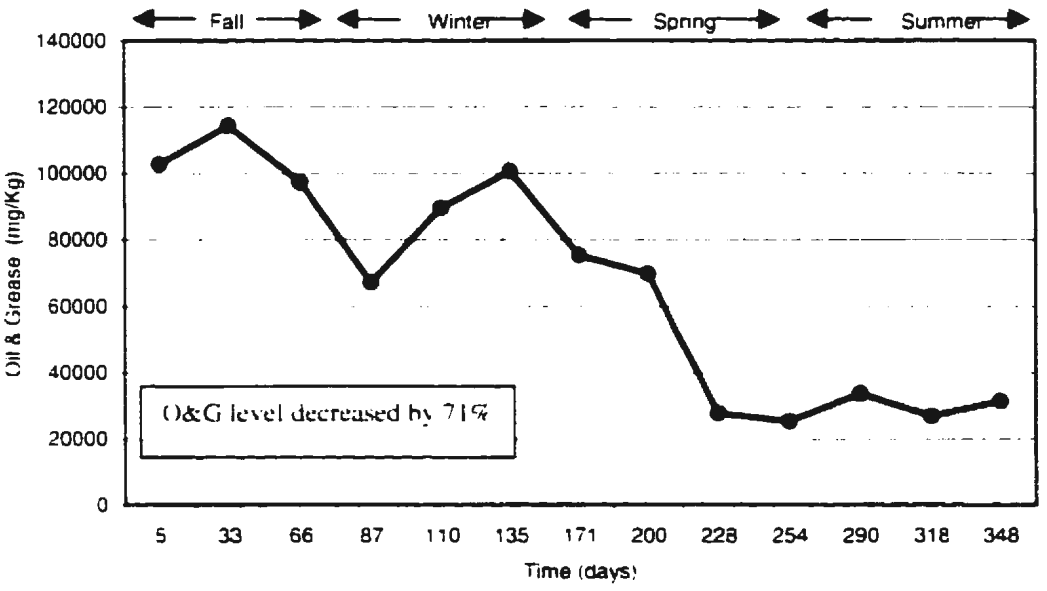

Figure 4.21 Oil and Grease concentrations versus time for LF3

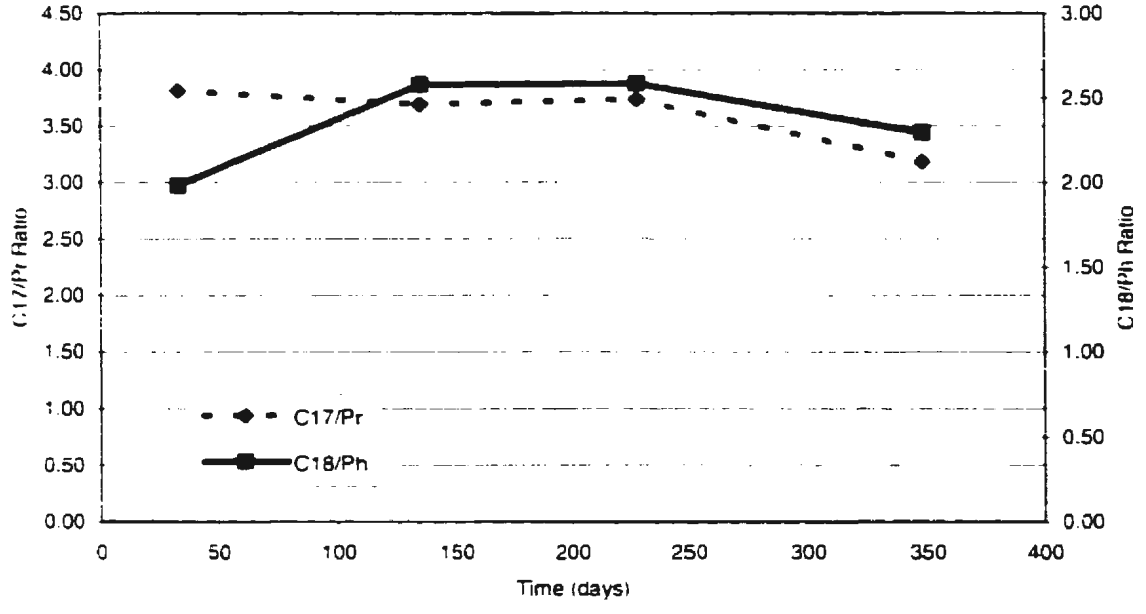

Figure 4.22 C_{17}/Pr and C_{18}/Ph ratios versus time for LF3

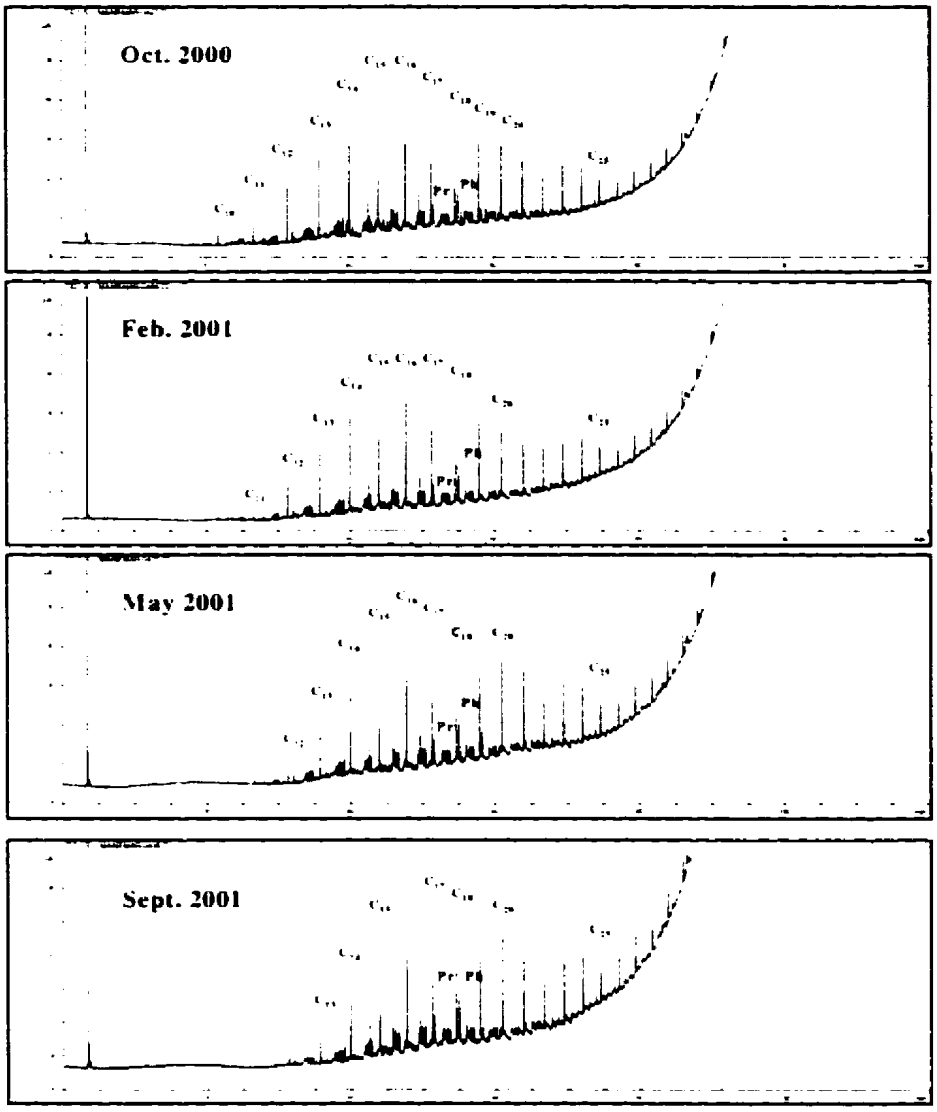

Figure 4.23 Gas chromatograph of LF3 sludge samples collected on Oct 2000, Feb 2001, May 2001 and Sep 2001

4.6.4 LF4 (Tilling + Nutrient)

The intent of LF4 was to study the kinetics of oily sludge degradation in a landfarm under enhanced conditions where fertilizers and tilling were applied.

Even though this cell was not watered, the moisture content maintained a range between 8.5% and 1.3% (Table 4.4). The origin of this moisture was thought to be from the water in the sludge as well as the rain that occurred between November and December 2000. When the moisture content range was compared with that of LF1 (both were not watered), it is clear that the moisture content in LF1 was higher than LF4. This is mainly due to the fact that LF4 was tilled on a regular basis, which increased the evaporation rate in this cell. With the exception of the measured moisture content in June (1.3%), the moisture content throughout this study was sufficient to support the microbial activity (Section 4.3.5.1). It is interesting to note that the moisture content in LF4 during the summer period was higher than in LF2 (cell was tilled but not watered). This could be either due to the fact that the fertilizers acted as a liner (similar to a sponge) where it contained water and also minimized the evaporation effect, or that the soil became biologically enhanced and caused the formation of biofilms that retained the water inside them. Another possibility is that high fertilizer concentrations have an osmotic effect, which decreases the vapor pressure of water thereby reducing evaporation. Biofilms are created by bacteria and are largely composed of water, bacteria cells, bacteria secretion and inert particles. The water content of biofilms typically ranges from 87% to 99% (Characklis 1990). It was also noticeable that the soil became compacted and hard (consolidated) compared to the soil in the other cells, where during the sampling process

the soil was too hard to penetrate with the auger. The observed level of microbial counts was in the range of 3.9E+06 to 2.1E+12 GAB/g (Table 4.6), which is higher than the microbial range in LF1 (2.2E+06 to 2.2E+10 GAB/g). Although the measured microbial counts in March (2.1E+12 GAB/g) were high, such high counts have been reported in sludge from different sewage treatment plants (Curds and Hawkes 1975). Even though water was not added, it appears that the rain and moisture in the sludge were sufficient for biodegradation. The highest microbial count was measured in this cell during the month of March. This high level occurred during the time when the bacteria were active as their number was increasing due to the availability of food (hydrocarbon), the presence of fertilizers that enhanced the soil, and the presence of water. Throughout this study, the bacterial counts in this cell were above the required level to support the biodegradation process (Morgan et al. 1989; Arora et al. 1982).

The total reduction in O&G concentration in LF4 was approximately 40% (Figure 4.24). This was the lowest reduction among all nine cells. The concentrations between days 5 and 135 did not follow any consistent trend (increasing and decreasing intermittently). From day 135 until day 254, the concentrations followed a consistent decreasing trend where O&G concentration dropped from 66,460 to 20,033 ppm. Following this period, O&G levels increased significantly from 20,033 to 38,230 ppm, after which they leveled off within the range of 37,290 to 41,255 ppm. It appears that the addition of fertilizers without being dissolving in water caused the soil to be compacted, which resulted in the formation of localized soil and sludge clusters with an uneven distribution of sludge in the cell. The inconsistency in the data might be due to this phenomenon.

The ratios of C17/pristane and C18/phytane were plotted against time (Figure 4.25) to determine the extent of biodegradation. LF4 showed a sharp decrease in C17/pristane and C18/phytane ratios which occurred between October 2000 and February 2001 (C17/pristane ratio was 2.97 in October 2000 and 0.26 in February 2001 and the C18/phytane ratio was 1.75 in October 2000 and 0.2 in February 2001, Table 4.3), indicating that most of the n-alkanes had degraded in the first five months. Since LF4 showed a sharp decrease in its n-alkanes and at the same time its branched alkanes such as pristane and phytane mostly remained intact, this indicates that the disappearance of these compounds is mainly due to biodegradation and not weathering. On the other hand, most of the decrease in the O&G took place between February and June (from 66,460 to 20,033 ppm). During this time, and as evident from Figures 4.25 and 4.26, biodegradation did not take place. This indicates that weathering was the dominant degradation process in this cell during this period. It is also believed that the reason for this particular cell showing the lowest decrease in the O&G concentrations (40%) is that the addition of fertilizer without the addition of water caused the topsoil to become hard and thus minimized the weathering effect.

Summary

From the above findings, it is concluded that both biodegradation and weathering occurred in LF4. When the biodegradation process in LF4 was compared to those of LF1, LF2 and LF3, it was clear that biodegradation was much more active in LF4 than in the other cells. The only difference in the treatments between LF4 and the other three cells

was the addition of fertilizers to LF4. From this, it can be concluded that fertilizers are a key element to stimulate and enhance the biodegradation process. However, when the weathering process in LF4 was compared with the other cells, it was obvious that this effect was much less in LF4, and this is believed to be due to the addition of fertilizers without adding water.

The extent of the biodegradation in LF4 can be classified as moderate with a rank between 3 to 4 (Peters and Moldowan 1993).

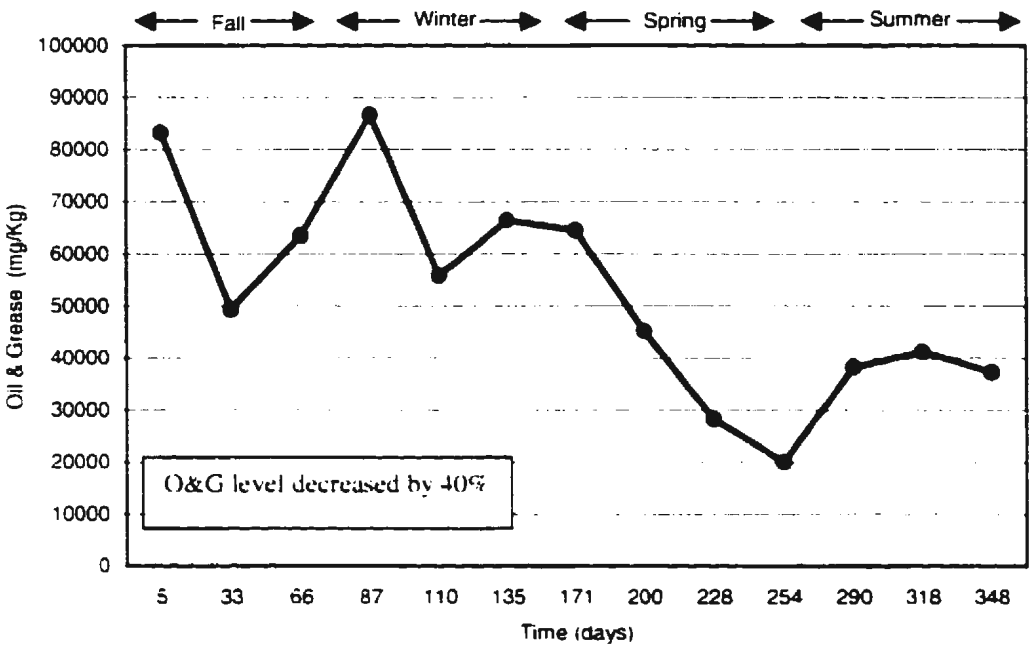

Figure 4.24 Oil and Grease concentrations versus time for LF4

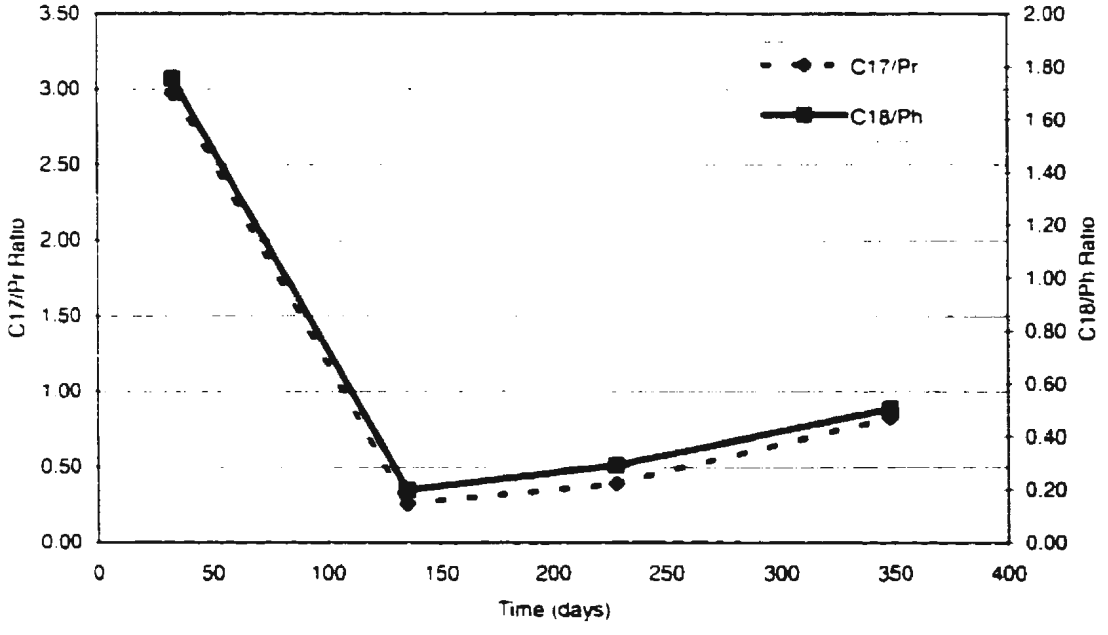

Figure 4.25 C17/Pr and C18/Ph ratios versus time for LF4

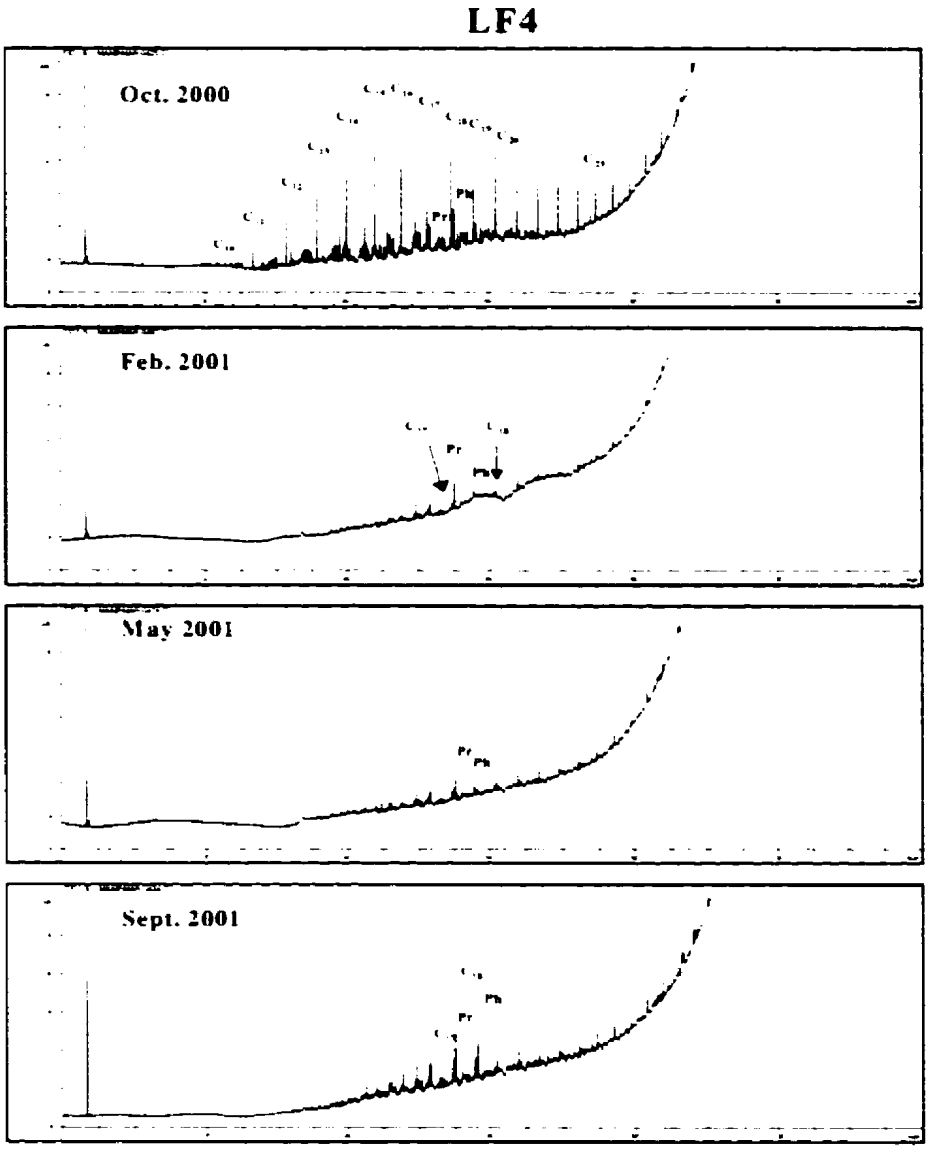

Figure 4.26 Gas chromatograph of LF4 sludge samples collected on Oct 2000, Feb 2001, May 2001 and Sep 2001

4.6.5 LF5 (Tilling + Nutrient + Water)

The intent of LF5 was to study the kinetics of oily sludge degradation in a landfarm under enhanced conditions where tilling, fertilizers and water were applied.

The moisture content range in LF5 during this study was between 10.6% and 1.7% (Table 4.4). Despite the weekly watering of this cell during the summer season, the moisture content in LF5 was lower than in LF1, which was not watered. This is mainly due to the high evaporation rate, which was enhanced by the tilling activities. A noticeable drop in the moisture content level took place between May and July 2001 (from 5.0% to 1.7%); however, this level increased to 3.3% by September 2001. The observed level of microbial counts was in the range of 3.9E+05 to 2.3E+10 GAB/g (Table 4.6), which is also close to the range of microbial counts in LF1 (2.2E+06 to 2.2E+10 GAB/g). The lowest microbial counts occurred in July 2001, which is also the same period at which the moisture content was at its lowest level. When the moisture content started to increase (August and September 2001), the microbial counts increased from the low level of 3.9E+05 GAB/g to 8.7E+08 GAB/g. Throughout the study, the moisture level in LF5 was sufficient to support the microbial activity, and the microbial counts were above the level required to perform the biodegradation process (Arora et al. 1982; Morgan et al. 1989).

The total reduction in the O&G concentrations in LF5 was approximately 75% (Figure 4.27). This was the second largest drop in the O&G level after LF2. During the initial phase of the study (first month), the O&G concentrations increased slightly from 102,373 to 117,380 ppm; however, these concentrations started to decrease steadily from day 33

(117,380 ppm) and continued until day 254 (23,190 ppm) after which they leveled off within the range of 23,703 to 27,033 ppm. This cell showed a smooth downward trend for the decrease in its O&G concentrations.

The ratios of C17/pristane and C18/phytane were plotted against time (Figure 4.28) to determine the extent of biodegradation. This plot was similar to that of LF4. However, LF5 showed a sharp decrease (not as sharp as in LF4) in C17/pristane and C18/phytane ratios between October 2000 and May 2001 (C17/pristane ratio was 2.83 in October 2000 and 0.2 in May 2001; the C18/phytane ratio was 1.78 in October 2000 and 0.17 in May 2001, Table 4.3), indicating that most of the n-alkanes had degraded in the first nine months. The gas chromatograph for the n-alkanes of LF5 (Figure 4.29) also showed the disappearance of most of the n-alkanes by May 2001. Since LF5 showed a big drop in its n-alkanes and at the same time its branched alkanes such as pristane and phytane mostly remained intact, this again indicates that the disappearance of these compounds was mainly due to biodegradation and not weathering.

Summary

The decrease in O&G concentrations (75%) in LF5 is due to both weathering and biodegradation. Since biodegradation only occurred to the n-alkanes, which represents one of many groups of the saturate and since the saturate represents less than 35% of the hydrocarbon groups in this sludge (see Section 4.2.2), it is clear that the majority of the O&G loss is due to weathering. The extent of the biodegradation in LF5 was similar to that in LF4, which can also be attributed to the addition of fertilizers. Since the

weathering effect, as shown in the other cells, did not start until day 135, the early degradation trend in this cell is attributed to the biodegradation process. The overall drop in the O&G level is the combined effect of both weathering and biodegradation. To determine the contribution of each of these two processes to the whole degradation process, further work is required.

The extent of the biodegradation level can be classified as moderate with a ranking of 4 (Peters and Moldowan 1993).

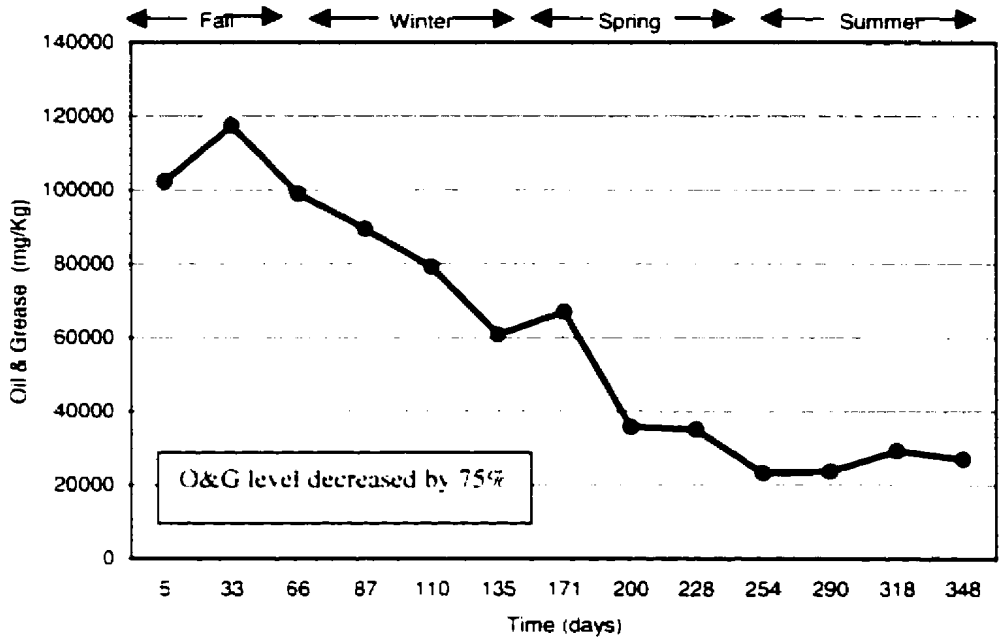

Figure 4.27 Oil and Grease concentrations versus time for LF5

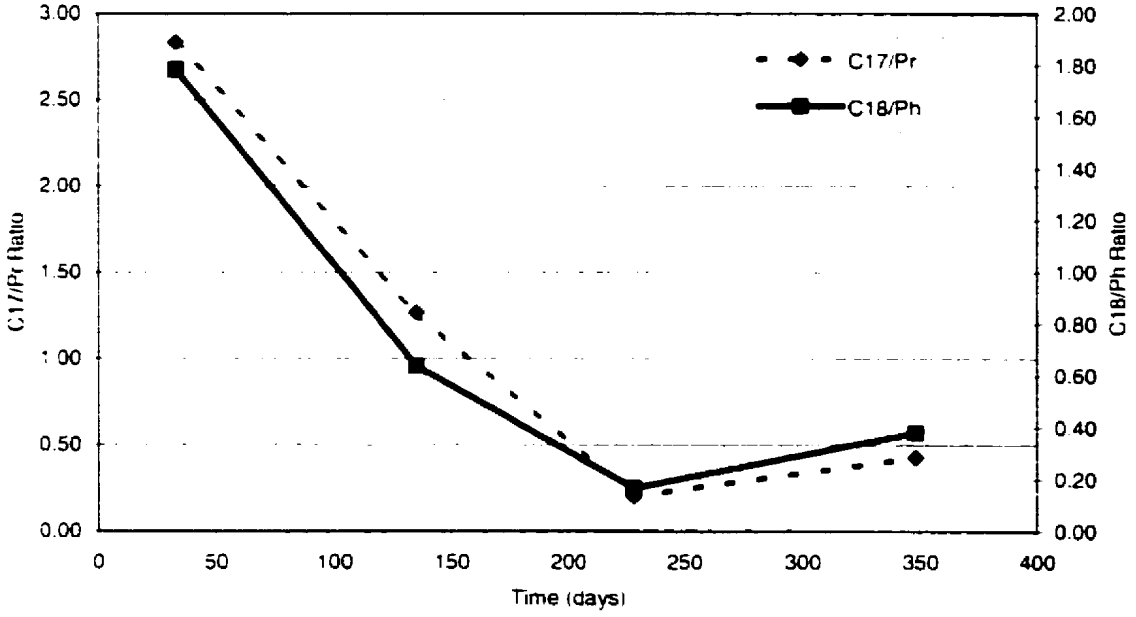

Figure 4.28 C_{17}-/Pr and C_{18}/Ph ratios versus time for LF5

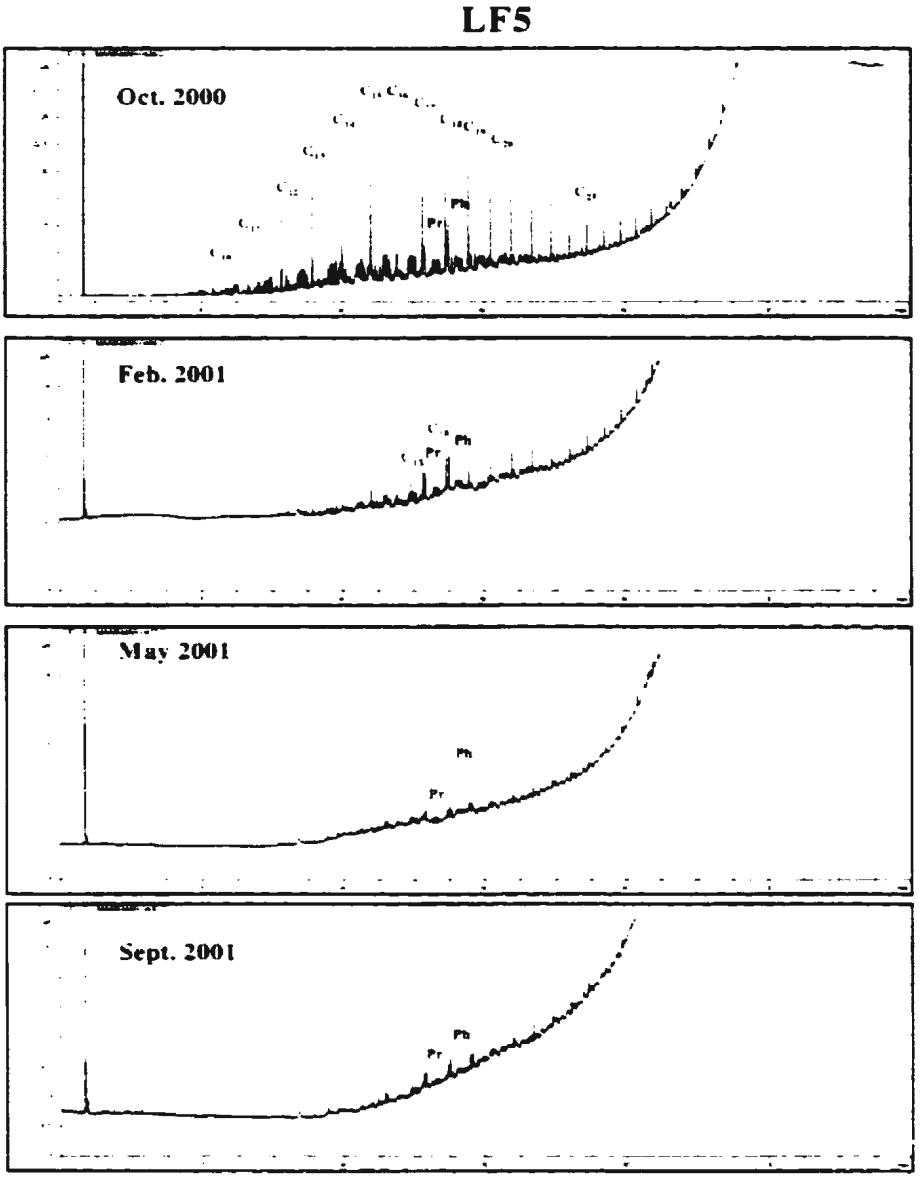

Figure 4.29 Gas chromatograph of LF5 sludge samples collected on Oct 2000, Feb 2001, May 2001 and Sep 2001

4.6.6 LF8 (Tilling + Nutrient + Water + Loading Rate)

The intent of cell LF8 was to assess the effect of increasing oily waste loading under arid conditions where tilling, fertilizers and water were applied.

In order to make the most effective use of a landfarm, the highest loading rate of the hydrocarbon is desired. The literature recommended that the loading rate of the hydrocarbon should be between 0.05 and 0.10 kg of sludge per kg of soil (Jenson 1975; Concawe 1980; Brown 1981; Huesemann 1994). Since this study was carried out in an arid region, it was decided to use one of the cells (LF8) to evaluate the effect of doubling the loading rate on the degradation process. The amount of applied sludge on LF8 was 700 kg (0.28 kg of sludge per kg of soil) while each of the other cells received 350 kg of sludge (0.14 kg of sludge per kg of soil). The sludge was applied to LF8 on September 21, 2000 and the O&G concentration, as measured on September 26, 2000, was 181,770 ppm.

The moisture content range in LF8 during this study was between 11.4% and 7.0% (Table 4.4). This range was higher than that in all of the other cells including LF5, which had identical treatment to LF8 with the exception of the loading factor. The evaporation rate as well as the tilling activities did not lower the moisture content in this cell below 7%. Apparently the high concentration of hydrocarbons acted to minimize the evaporation rate. The observed level of microbial counts was in the range of 2.3E+05 to 2.3E+12 GAB/g (Table 4.6), which is close to the range of LF5. It was noticed that the lowest microbial counts in this cell were measured at the beginning of the study (September

2000); they were also the lowest initial microbial counts among all other cells. The highest microbial counts were measured in March 2001, the period when most of the other cells also showed their highest microbial counts. At the beginning of the hot season (April), the microbial counts dropped from 10^{12} to 10^{6}. Since the moisture in the soil during this time was high (>8%), this decrease is believed to be mainly due to the high temperatures. These counts stayed almost constant until the end of the study when they started to increase again in the cooler months.

The total reduction in the O&G concentration in LF8 was approximately 58% (Figure 4.30). Initially, O&G levels dropped from 181,770 to 156,143 ppm, between days 5 and 33. Between days 33 and 171, the concentrations appeared to have leveled off in the range of 158,620 and 147,700 ppm. The drop in O&G in this cell started at day 171 (158,620 ppm) and continued until the beginning of the summer season (72,377 ppm), after which there was hardly any change in these concentrations. This drop is mainly due to the weathering effect; however, the delay in this drop, as compared to the other cells, was mainly due to the high loading rate. It was observed that during the period between days 33 and 171, when the O&G levels were almost at a steady state, the number of microbes increased significantly (from 10^{5} to 10^{12}), causing biodegradation to take place.

The ratios of C17/pristane and C18/phytane were plotted against time (Figure 4.31) to determine the extent of biodegradation. LF8 showed a steady decline in C17/pristane and C18/phytane ratios occurring between October 2000 and September 2001 (the C17/pristane ratio was 3.21 in October 2000 and 0.81 in September 2001; the

C18/phytane ratio was 2.01 in October 2000 and 0.49 in September 2001, Table 4.3), indicating that the n-alkanes were degraded, although at a slower rate than in LF4 and LF5. This is also observed from Figure 4.32, where a significant decrease in the n-alkanes is shown to have taken place between May and September 2001 and at the same time the branched alkanes such as pristane and phytane mostly remained intact. Figure 4.32 also showed that preferential weathering of light ends C10 and C11 n-alkanes took place by February 2001. Since the volatilization rates for these compounds are greater than their microbial degradation rates (Salanitro 2001), this indicates that the disappearance of these compounds at the beginning of the study was mainly due to weathering. The decrease in O&G between days 5 and 33 also supports this, especially since no significant biodegradation occurred at this time.

Summary

The following are the key findings from LF8:

- The high loading rate resulted in retaining a high moisture content in the soil.
- Unlike other cells, the high loading rate in this cell prevented the weathering process (evaporation) for a long period (between days 5 and 171).
- One of the field observations was that the oil has formed tar-like balls with the soil that affected cell operations and sampling. The formation of these balls probably prevented degradation at an early stage and reduced the weathering rate.
- The high loading rate caused bacterial counts to increase, as it provided them with a plentiful source of food and water; however, it did not stimulate them to start the

biodegradation process until a lapse of seven months, unlike LF4 and LF5 where the biodegradation started almost immediately.

From all of the above findings, it is concluded that degradation of O&G occurred despite the high loading rate in LF8 and that this degradation was due to both weathering and biodegradation.

The extent of the biodegradation level can be classified as light to moderate with a rank between 3 and 4 (Peters and Moldowan 1993).

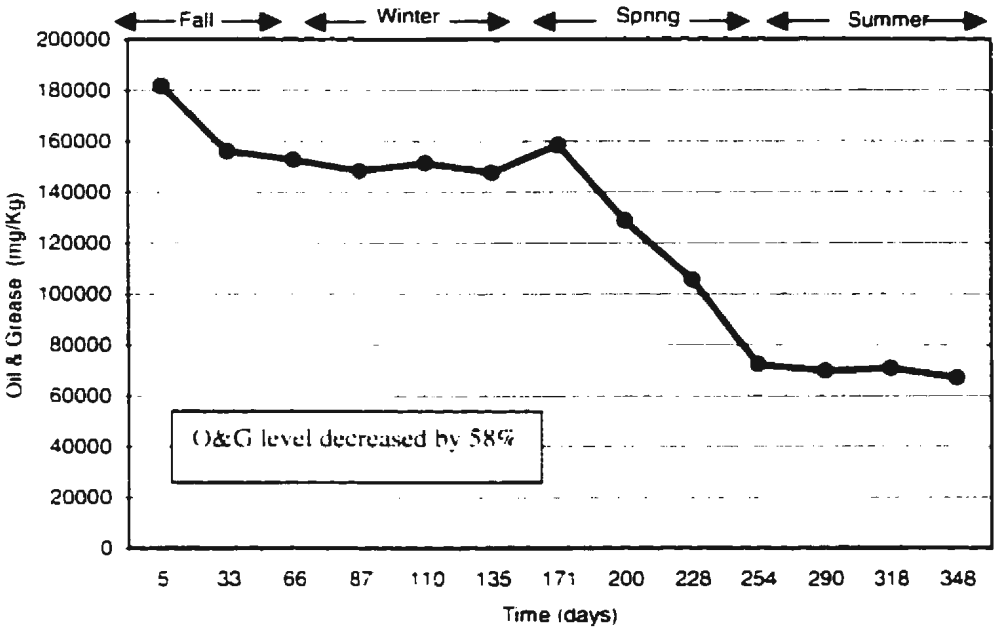

Figure 4.30 Oil and Grease concentrations versus time for LF8

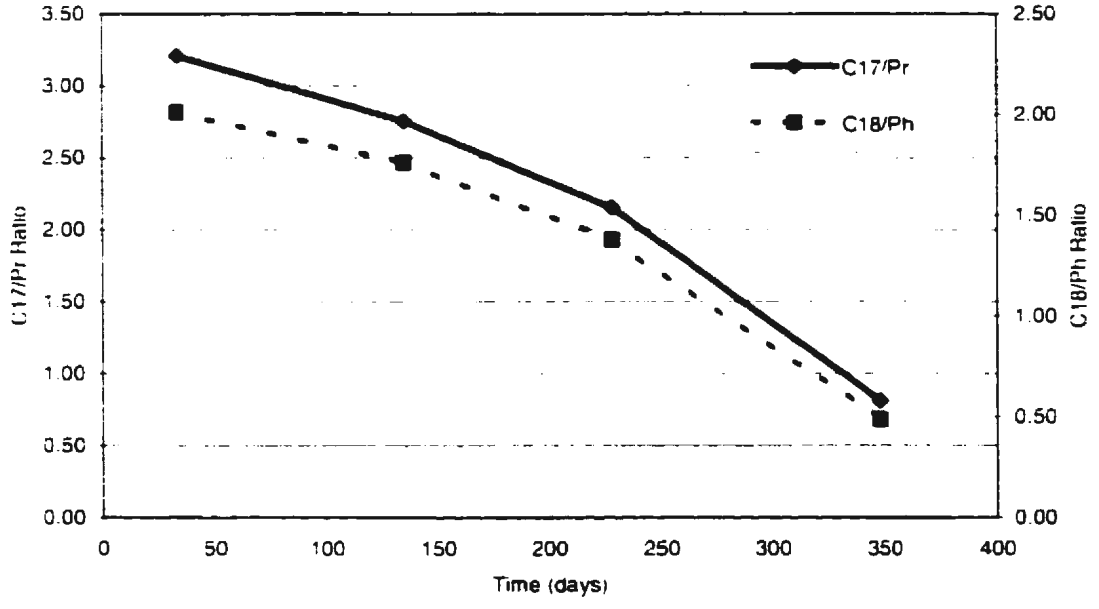

Figure 4.31 C_{17}/Pr and C_{18}/Ph ratios versus time for LF8

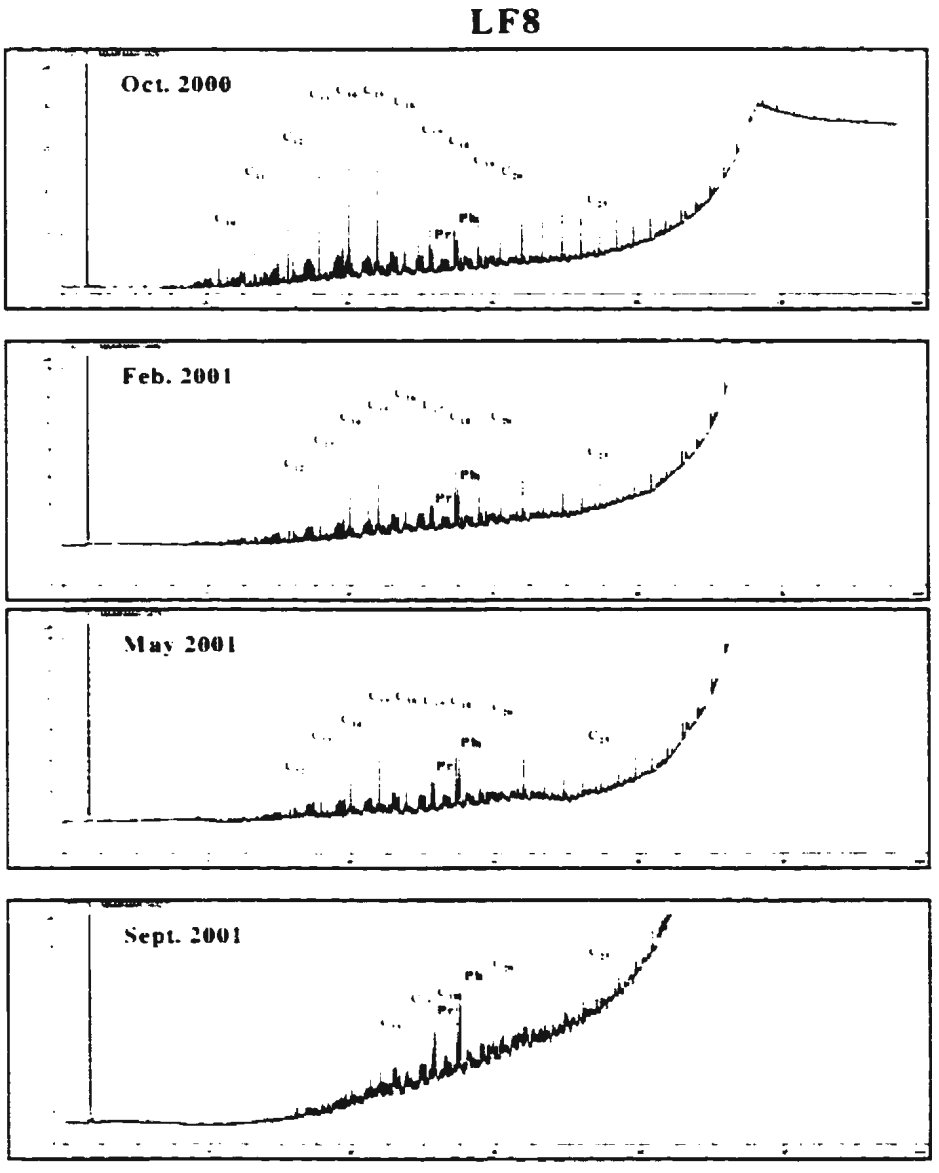

Figure 4.32 Gas chromatograph of LF8 sludge samples collected on Oct 2000, Feb 2001, May 2001 and Sep 2001

4.6.7 BR2 (Air + Nutrient + Water + Cover)

The intent of BR2 was to study the kinetics of oily sludge degradation in a closed system known as a bioreactor where air and water in addition to the fertilizers were injected mechanically. The level of degradation in a bioreactor will be compared with an equivalent landfill cell (LF5).

Four cells (BR1, BR2, BR3, & BR4) were constructed using a similar design as that used by McNicoll et al. (1995) and were monitored to determine the efficiency of the bioreactor system and to compare their performance with the landfarm cells that had similar treatments (BR2 and BR3 versus LF5, and BR4 versus LF1).

The moisture content range in BR2 during this study was between 10.5% and 3.2% (Table 4.4), which was sufficient to support microbial activities. When the range of moisture content between BR2 and all landfarm cells were compared, it was clear that the range in BR2 was much higher than that in all landfarm cells with the exception of LF8. When comparing the moisture content between BR2 and LF5 (both cells had similar treatments in terms of adding water, fertilizers and aeration; however, BR2 had a cover while LF5 did not), it is also obvious that the moisture content in BR2 was much higher than that in LF5 except when the rain occurred between November and December 2000. The observed levels of microbial counts in BR2 were in the range of 2.1E+07 to 2.3E+12 GAB/g (Table 4.6). This range was one of the highest measured in this study. It was also noticed that the cover was effective in minimizing the evaporation effect (as indicated by

the high moisture content in the cell). The treatment (adding water and air mechanically) was also effective, as indicated by the high level of microbial counts.

As shown in Figure 4.33, the total reduction in O&G concentrations in BR2 (69%) was less than the total reduction in LF5 (75%). This was expected because unlike other cells BR2 had a cover and was not tilled, both of which minimized the evaporation process. Between days 5 and 228, there was a decreasing trend in O&G concentrations; however this trend was not consistent as there were periods where the concentrations increased and decreased intermittently. The O&G concentration on day 5 was 87,040 ppm and on day 228 it was 19,640 ppm. The sharpest decrease took place between days 171 and 228 where the concentrations decreased from 70,700 to 19,640 ppm, after which they leveled off within the range of 25,147 - 27,435 ppm. Based on the trend of the O&G decrease, the measured concentration in February (54,550ppm) and in May (19,640 ppm) appeared to be low.

The ratios of C17/pristane and C18/phytane were plotted against time (Figure 4.34) to determine the extent of biodegradation. There were three distinct trends that could be observed from the C17/pristane and C18/phytane plotted ratios. The first occurred between October 2000 and February 2001 where there was a sharp decrease in these ratios (C17/pristane ratio was 3.18 in Oct. 2000 and 1.75 in February 2001; the C18/phytane ratio was 1.99 in October 2000 and 1.07 in February 2001, Table 4.3). The second trend showed a moderate decrease between February and May 2001, followed by a third trend where these ratios appeared to have leveled off. The first two trends indicate

that biodegradation occurred between the start of the study until May 2001, after which the degradation process became slow. It was also observed that at the same time when the biodegradation started to level off (May), the O&G concentration was at its lowest and the moisture content started to decrease.

The gas chromatograph for the n-alkanes of BR2 (Figure 4.35) showed that by February 2001, the light ends (C10, C11 and C12 n-alkanes) disappeared and that other n-alkanes (up to C25) also decreased. Since the weathering process was minimized by the cover and the absence of tilling, and since all of the n-alkanes had either disappeared completely or partially by February 2001, this is a clear indication that biodegradation was the dominant degradation process in this cell during the first five months of the study. Another observation to support this conclusion is that the decrease in the O&G concentrations up to February 2001 was small (approximately 7%). If weathering was the dominant degradation process, the decrease in O&G would have been much higher as in LF5 which showed a decrease in the O&G concentrations of about 23% for the same period. Between March and September 2001, the O&G concentrations decreased by approximately 64%. This decrease was mainly due to weathering which resulted from the increase in temperature from the beginning of the spring season and continuing through the whole summer. It was also observed from the field that despite the attempts to close the holes that were drilled during the sampling activities (three to four holes were drilled every month) with clay, the surface of the cell started to crack, and this probably increased the effect of evaporation. The weathering process became the dominant

degradation process in BR2 starting April 2001. The decrease in the n-alkanes continued during May 2001 but at a reduced rate.

Summary

The decrease in O&G concentrations (69%) in BR2 is due to both weathering and biodegradation. The existence of a cover in the absence of tilling operations prevented the weathering process from taking place at the early stage (first five months). As the temperature started to increase (April) and as the cover started to crack, the weathering process became the dominant degradation process in this cell. The biodegradation process in BR2 appeared to have been slower than that in LF5. The extent of the biodegradation that took place at the beginning of the study can be classified as light with a rank of 3 (Peters and Moldowan 1993).

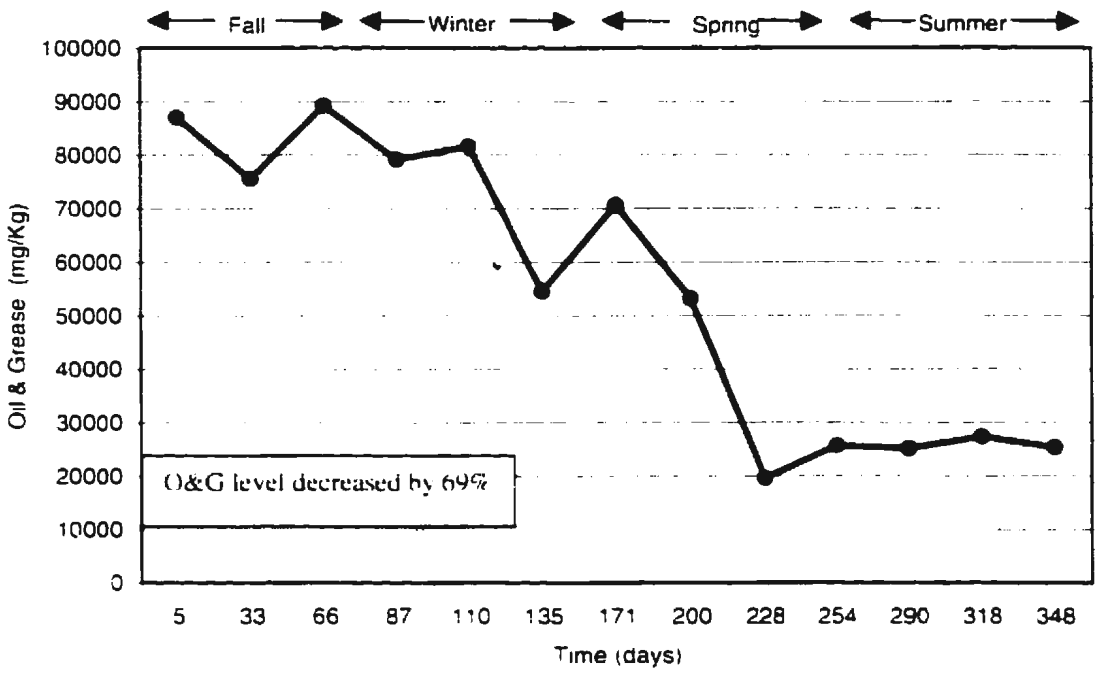

Figure 4.33 Oil and Grease concentrations versus time for BR2

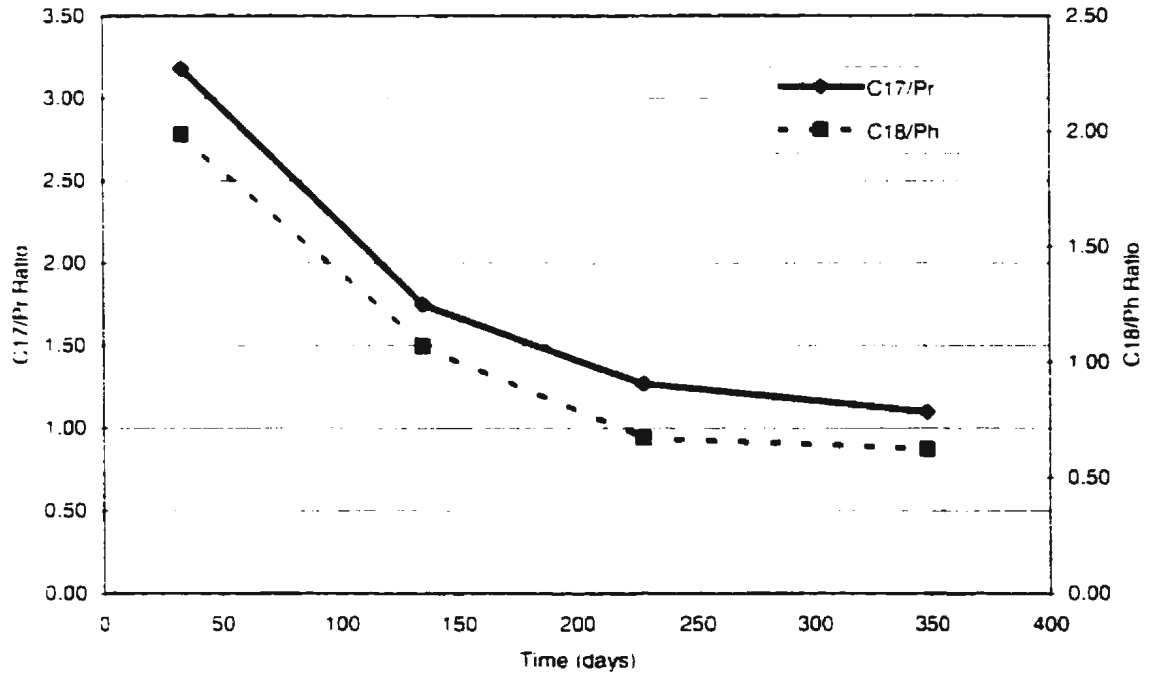

Figure 4.34 C_{17}/Pr and C_{18}/Ph ratios versus time for BR2

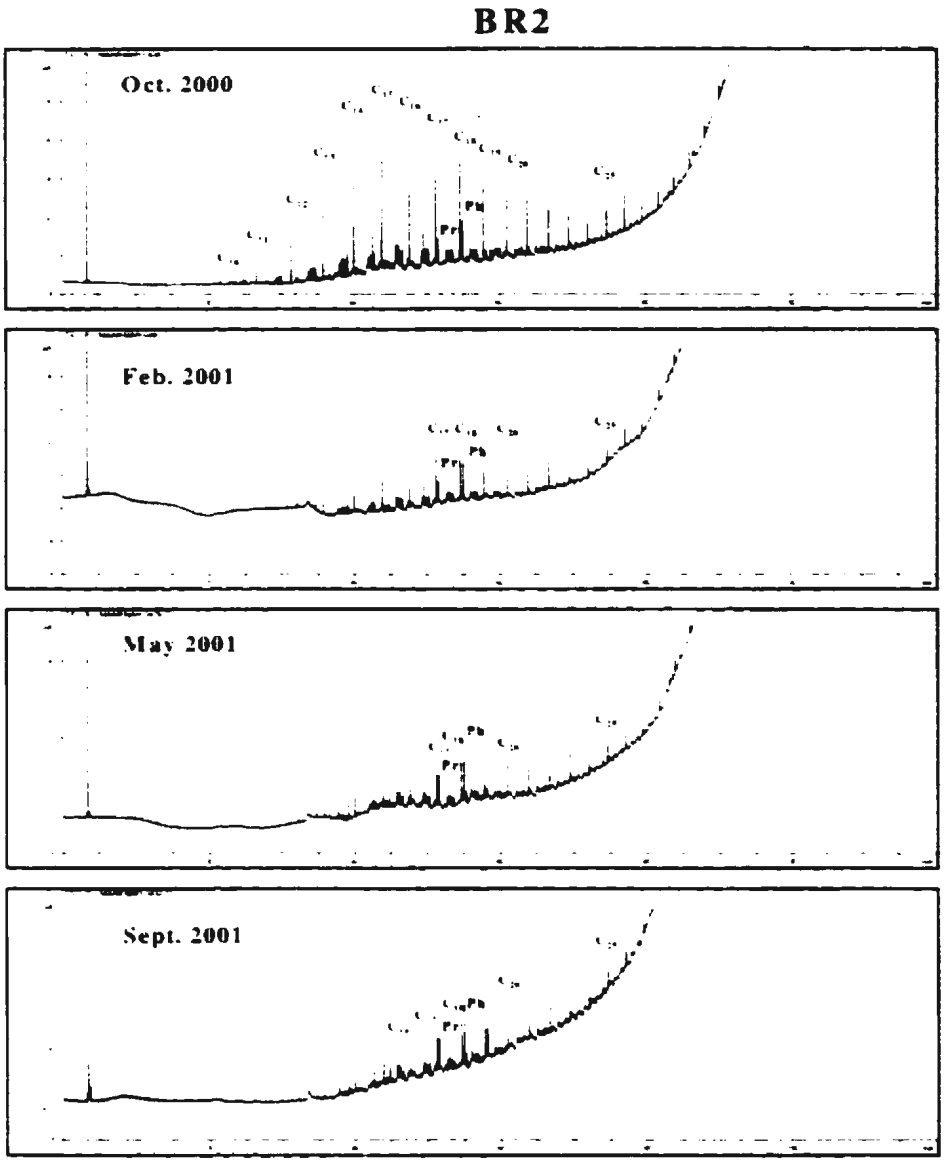

Figure 4.35 Gas chromatograph of BR2 sludge samples collected on Oct 2000, Feb 2001, May 2001 and Sep 2001

4.6.8 BR3 (Air + Nutrient + Water + No Cover)

The intent of BR3 was to study the kinetics of oily sludge degradation in an open bioreactor system, where air and water were injected mechanically in addition to the fertilizers, and to compare its performance with BR2 and LF5.

The treatment applied to BR3 was exactly the same as to BR2, except that BR3 was not covered with a clay layer while BR2 had a cover on the top. This treatment was also the same as that applied at LF5 with the exception that watering and aerations were applied mechanically to BR3, while watering and aerations were applied manually in LF5. The moisture content range in BR3 during this study was between 7.5% and 1.7% (Table 4.4), which was sufficient to support microbial activities. When comparing the range of moisture content between BR3 (7.5% and 1.7%) and BR2 (10.5% and 3.2%), it is clear that the moisture content in BR3 was less. This is mainly due to the absence of a cover. The observed level of microbial counts in BR3 was in the range of 2.1E+06 to 2.2E+12 GAB/g (Table 4.6). This range was also one of the highest (similar to BR2). The microbial counts were above the level required to perform the biodegradation process (Arora et al. 1982; Morgan et al. 1989). The high microbial counts indicated that the cell treatment (adding water and air mechanically) was effective.

The total reduction in O&G concentrations in BR3 was approximately 67% (Figure 4.36), which is very close to that of BR2 (69%). However, this reduction was less than the reduction in LF5 (75%). Since the bulk of the reduction in the O&G in BR3 was mainly due to weathering (see discussion on BR2) and since BR3 was aerated mechanically

through the perforated pipes and not through tilling, it is believed that the evaporation effect at BR3 was minimized and thus resulted in less reduction in its O&G levels compared to LF5. Between days 5 and 171, there was a general decreasing trend in O&G concentrations (from 89,628 to 63,655 ppm). The measured concentration in day 200 (70,365 ppm) was higher than day 171 (63,655 ppm). This was followed by a sharp decrease that occurred over a short period (i.e., days 200 and 228). However, from day 228 and onward, O&G concentrations leveled off within the range of 25,395 - 28,920 ppm. Based on the trend of the O&G decrease, the measured concentration in April (70,365 ppm) appears to be high.

The ratios of C17/pristane and C18/phytane were plotted against time (Figure 4.37) to determine the extent of biodegradation. The trends in this plot were similar to those from BR2, where three distinct trends were observed. The first occurred between October 2000 and February 2001 where there was a sharp decrease in these ratios (C17/pristane ratio was 3.61 in October 2000 and 2.06 in February 2001; the C18/phytane ratio was 2.2 in October 2000 and 1.34 in February 2001, Table 4.3). The second trend showed a moderate decrease between February and May 2001, followed by a third trend where these ratios appeared to have leveled off. The first two trends indicated that biodegradation occurred between the start of the study until May 2001, after which the degradation process became slow. It was also observed that at the time when the biodegradation started to level off in May, the O&G concentration was at its lowest level, and at the same time, the moisture content started to decrease.

The gas chromatograph for the n-alkanes of BR3 (Figure 4.38) was similar to that of BR2. Figure 6.38 shows that by February 2001, the light ends (C10, C11 and C12 n-alkanes) have disappeared and that other n-alkanes (up to C25) were decreasing. This is a good indication that biodegradation was taking place. The decrease in the O&G concentrations in BR3 (14%) between September 2000 and February 2001 was two orders of magnitude higher than the decrease of O&G in BR2 (7%) for the same period. Since both cells (BR2 and BR3) showed a similar decreasing trend in their n-alkanes as a result of biodegradation, the reason for the larger decrease in the O&G levels in BR3 was believed to be due to weathering. Between March and September 2001, the O&G concentrations have decreased by approximately 60%. This decrease is also due to weathering, which increased as a result of an increase in temperature. The weathering process became the dominant degradation process in BR3 starting from the spring season and the decrease in the n-alkanes continued throughout May 2001 but at a lower rate.

Summary

The decrease in O&G concentrations (67%) in BR3 is due to both weathering and biodegradation. When this decrease was compared to that in BR2 (69%), it was noted that the difference was insignificant indicating that the cover did not make a noticeable contribution to the degradation process. However, when the concentrations in BR2 and BR3 were compared to the concentrations in LF5 (75%), the difference became more apparent. From this it can be concluded that the weathering effect was minimized (in both BR2 and BR3) as a result of aeration of the cell by mechanical means instead of manual tilling. The biodegradation process in BR3 showed a similar profile to BR2 suggesting

that the cover did not have any effect. The biodegradation process in BR3, like BR2, appeared to have been slower than that in LF5. The biodegradation rank in BR3 can be classified as light with a rank of 3 (Peters and Moldowan 1993).

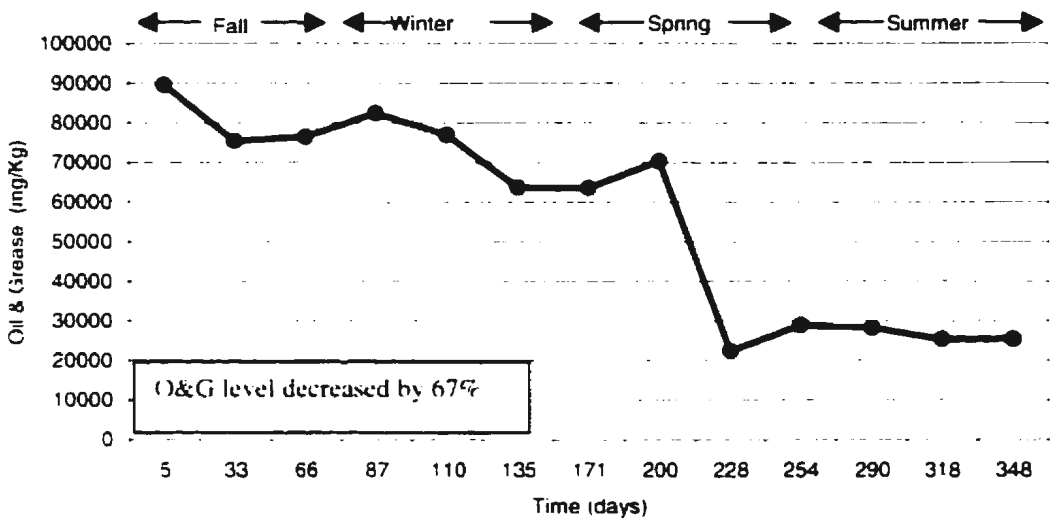

Figure 4.36 Oil and Grease concentrations versus time for BR3

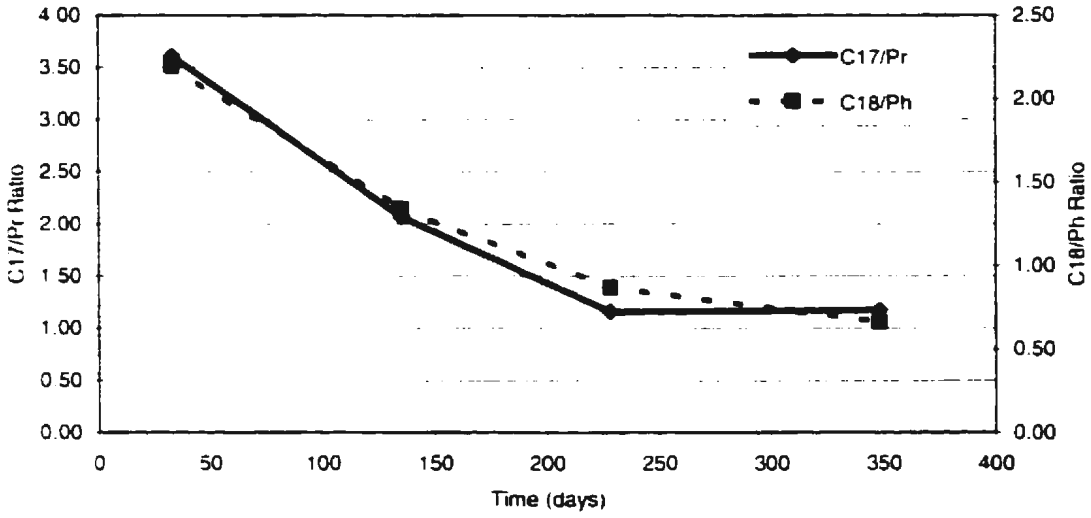

Figure 4.37 C_{17}/Pr and C_{18}/Ph ratios versus time for BR3

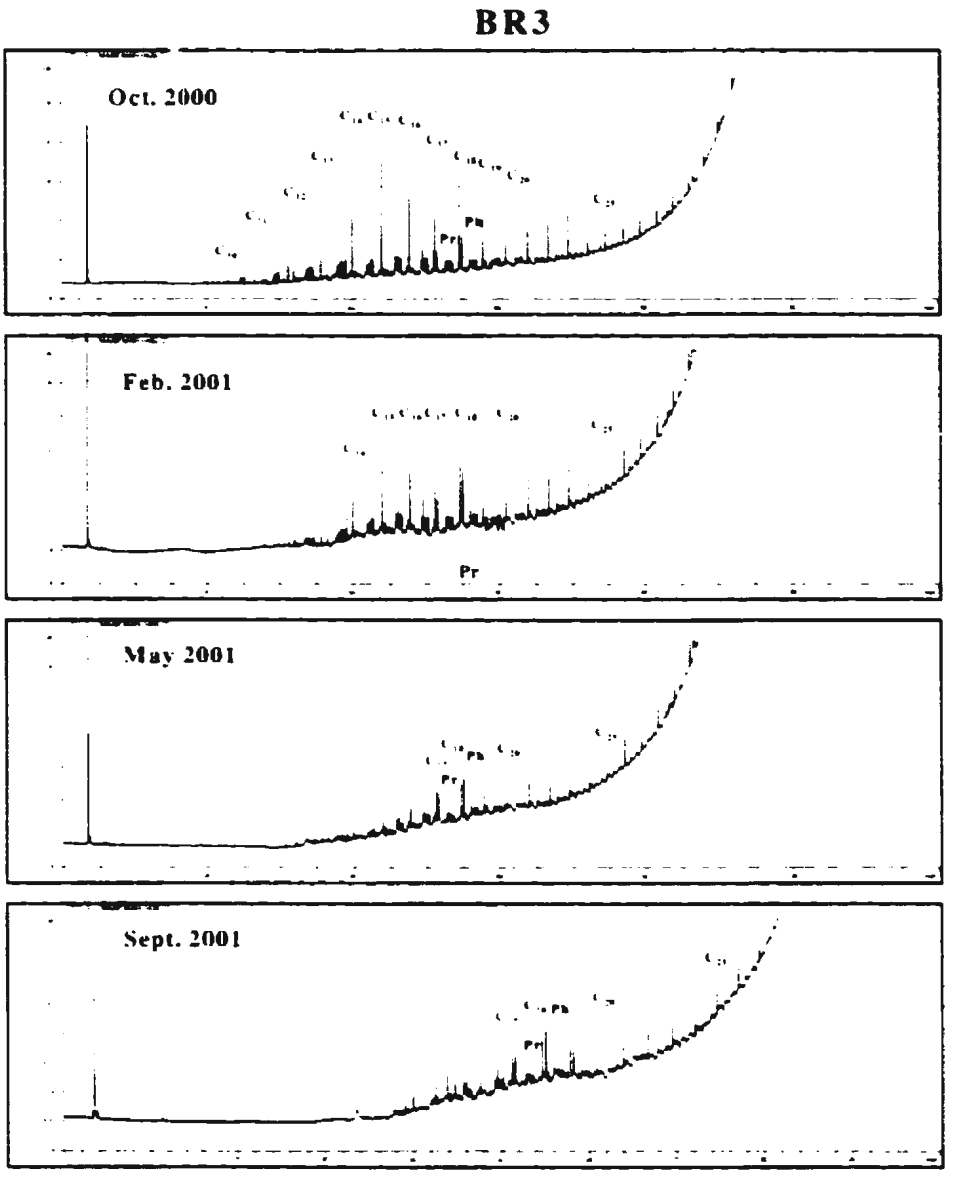

Figure 4.38 Gas chromatograph of BR3 sludge samples collected on Oct 2000, Feb 2001, May 2001 and Sep 2001

4.6.9 BR4 (No Action)

The intention of BR4 was to study the kinetics of oily sludge degradation in a closed bioreactor system under natural attenuation conditions (without the addition of water, air and nutrients), and to compare its performance with LF1.

The process of natural attenuation includes several components (biodegradation, sorption, dispersion, chemical reaction and volatilization), with biodegradation being regarded as the most important one (Swett 1998; US EPA 1999). For this study, no air, water or fertilizers were added to this closed cell.

The moisture content range in BR4 during this study was between 7.3% and 2.2% (Table 4.4), which was sufficient to support microbial activities. When the ranges of moisture content between BR4 (7.3% and 2.2%) and LF1 (9.7% and 3.0%) were compared, it appeared that the range in LF1 was slightly higher than that in BR4. This is probably due to the rainfall in November and December 2000, which increased the moisture content in LF1 but did not affect BR4 due to the presence of the cover. The observed level of microbial counts in BR4 was in the range of 3.9E+05 to 2.1E+12 GAB/g (Table 4.6). This range was higher than the range in LF1 (2.2E+06 to 2.2E+10 GAB/g).

The total reduction in O&G concentration in BR4 was approximately 65% (Figure 4.39). These concentrations appeared to have stayed almost constant without any significant changes between days 5 (91.775 ppm) and 171 (93.770 ppm). Following this period, the O&G concentrations declined significantly (from 93.770 to 29.063 ppm) in 60 days.

which coincided with the beginning of the summer season, after which the concentrations again leveled off within the range of 29,433 and 37,403 ppm. The decrease in the O&G level in BR4 appeared to have the same trend as that in LF1.

The ratios of C17/pristane and C18/phytane were plotted against time (Figure 4.40) to determine the extent of biodegradation. Since the calculated ratios of C17/pristane and C18/phytane in October 2000 were lower than those calculated in February, May and September 2001, it was decided to make the comparison between the ratios calculated in February 2001 and September 2001. The results showed that the ratios of C17/pristane and C18/phytane decreased slightly (the C17/pristane ratio was 4.11 in February 2001 and 3.69 in September 2001; the C18/phytane ratio was 2.78 in February 2001 and 2.36 in September 2001, Table 4.3), indicating that biodegradation was minimal. The gas chromatograph for the n-alkanes of BR4 (Figure 4.41) also showed that after one year, there were only small changes in the levels of n-alkanes. The only compounds that disappeared almost completely were the C10 n-alkanes. Other compounds that are known to have volatilization rates greater than their microbial degradation rates (Salanitro 2001), such as the C11 and C12 compounds, stayed intact, indicating that weathering was minimal. From this it can be concluded that the disappearance of these compounds is thought to be mainly due to volatilization and that the biodegradation effect is minimal. The decreases in the n-alkanes and the C17/pristane and C18/phytane in BR4 are similar in their profiles to those in LF1.

Summary

The degradation process in BR4 was mainly attributed to weathering with little biodegradation. The decrease in O&G concentrations in BR4 (65%) was more than the decrease in LF1 (57%). This was not expected especially since with BR4 covered the weathering process should have been minimized. However, it is believed that this high O&G is mainly due to the high loading rate in LF1 compared to BR4 (the initial O&G measured concentration in LF1 was 134.747 ppm, while in BR4 at the same time it was 91.775 ppm). It is very clear that both LF1 and BR4 have similar degradation profiles. From all these findings, it is concluded that natural attenuation, as demonstrated in BR4, should not be used as an on-going treatment/disposal method for oily sludge mainly because it takes a longer time to achieve the targeted treatment goals compared to the enhanced treatment methods (degradation in BR4 is expected to even take a longer time than LF1 mainly because of the cover which will result in minimizing the weathering effect).

The n-alkanes in general were still intact and the minimal biodegradation can be classified as light with a rank of 1 (Peters and Moldowan 1993).

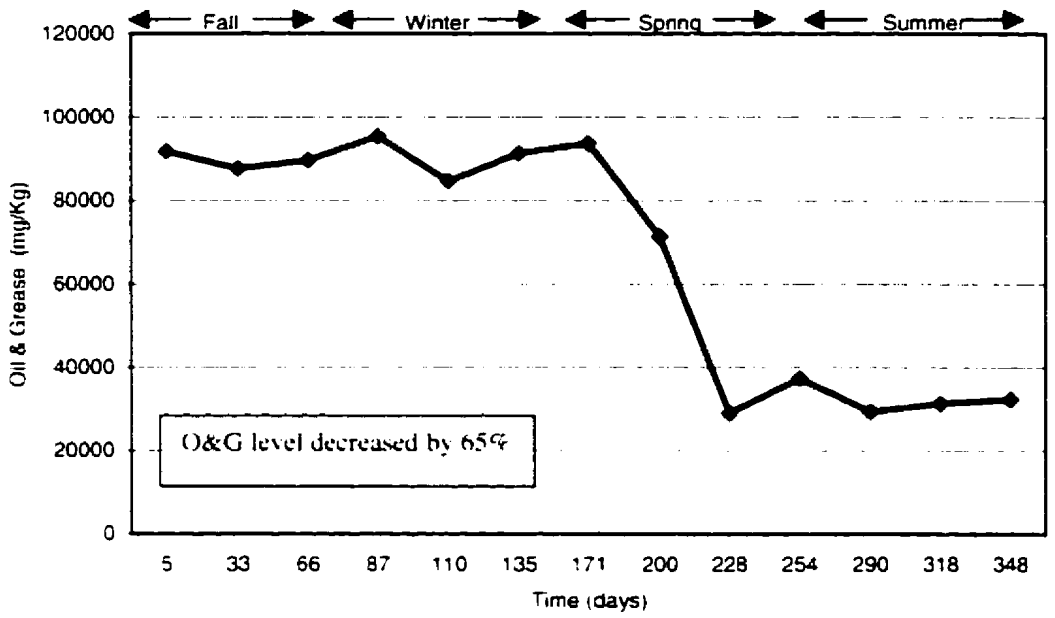

Figure 4.39 Oil and Grease concentrations versus time for BR4

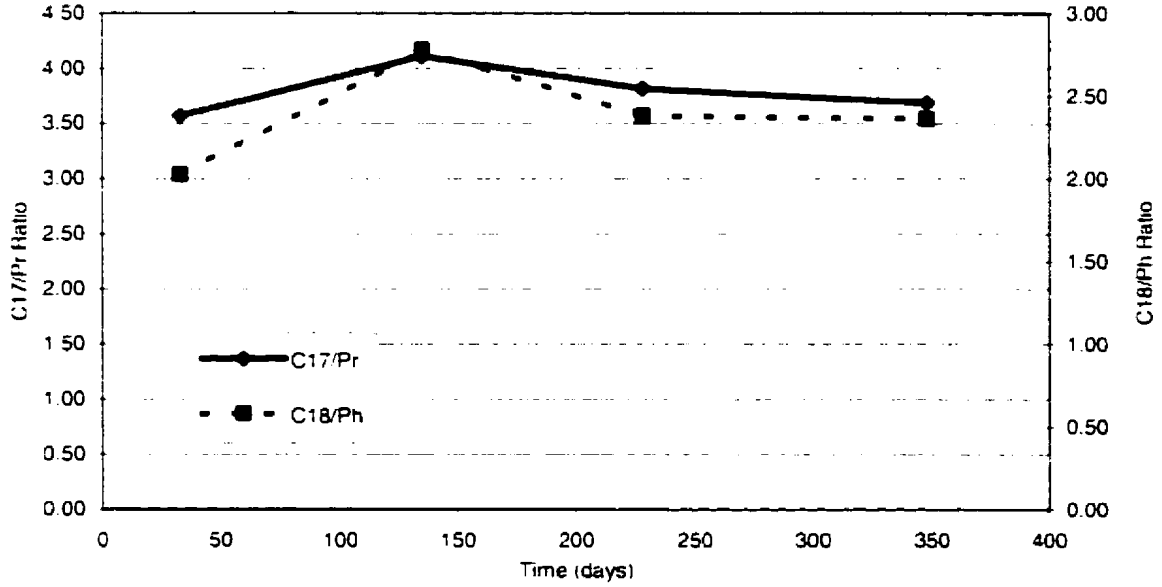

Figure 4.40 C_{17}/Pr and C_{18}/Ph ratios versus time for BR4

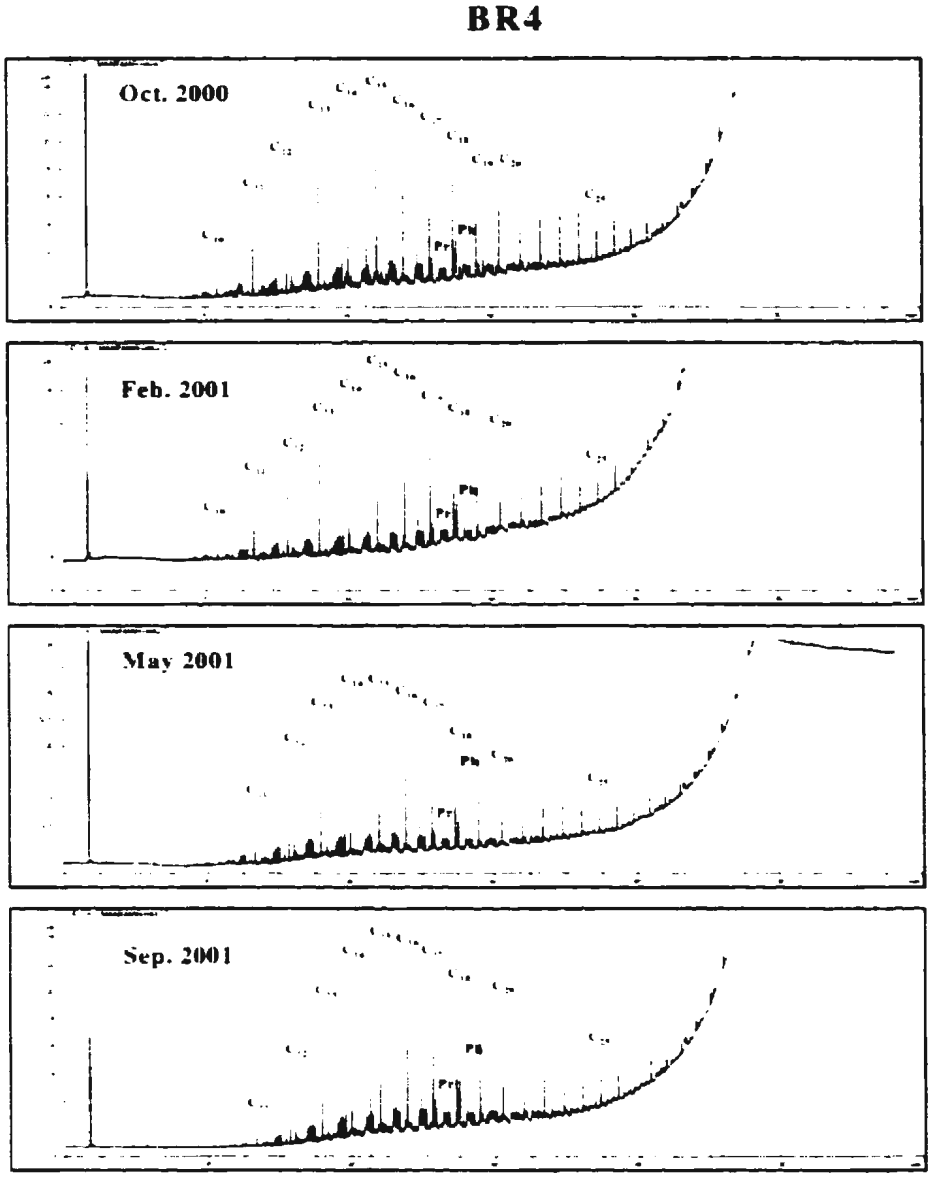

Figure 4.41 Gas chromatograph of BR4 sludge samples collected on Oct 2000, Feb 2001, May 2001 and Sep 2001

4.7 Two Stage Bio-Treatment System (BR1 and LF6)

One of the objectives of this research was to evaluate the effectiveness of combining both landfarm and bioreactor systems (a two-stage bio-treatment system) for accelerating oily waste biodegradation.

The idea for combining both systems was based on recommendations by Brown et al. (1990), who stated in their discussion on the use of bioreactor systems for treating soil contaminated with hydrocarbons that the bioreactor is twice as effective as conventional landfarming. In their discussion, they suggested that a combined bioreactor and landfarm system would be successful in reducing the hydrocarbons from a percentage level (in the landfarm) to low ppm levels (in the bioreactor); however, none of the literature reported any such attempt at this process in the field conditions.

Two cells (LF6 & BR1) were constructed as part of this study to evaluate the effectiveness of combining both landfarm and bioreactor systems. In the first stage, the intent was to place the sludge inside LF6 in order to achieve a gross reduction in the hydrocarbon by reducing the percentage of oil content by 75% to 80%. In the second stage, the intent was to remove the sludge, once the target reduction was achieved, from LF6 and place it inside BR1 to achieve a further reduction in hydrocarbons to low ppm levels.

The sludge was applied to LF6 at the same time as it was applied to all other cells (September 21, 2000); however, after six months (February 2001) it became clear that the

percentage reduction in the O&G was only 21% instead of the targeted range of 75% to 80% (the O&G concentrations in LF6 dropped from 118,065 ppm in September 2000 to 93,123 ppm in February 2001). As a result, it was decided to abandon this experiment before proceeding with the transfer of sludge to BR1.

4.8 Comparison Between Landfarm and Bioreactor Performance

The performances of the bioreactor and the landfarm cells with similar treatment were compared in order to determine which was the most effective treatment method. The comparison was conducted between landfarm cell LF5 and both bioreactor cells BR2 (with cover) and BR3 (no cover) since all of them received similar treatment in terms of adding water, fertilizers and aeration.

As concluded in the discussion on the performances of LF5, BR2 and BR3 (Section 4.6), degradation was an effective method for reducing the O&G levels in these cells. The landfarm cell (LF5) showed a total reduction in the O&G of about 75% while both BR2 and BR3 showed a total reduction of 69% and 67%, respectively. LF5 also showed a steady decrease in the O&G levels, while BR2 and BR3 showed a non-consistent decreasing trend (Figures 4.27, 4.33 and 4.36). Since the O&G reduction trends were not similar, this indicates that their weathering characteristics were different. These three cells were also among those that were classified as achieving the highest biodegradation rates (Figure 4.5).

When evaluating the data obtained from Sections 4.6.5, 4.6.7 and 4.6.8, the following conclusions were drawn:

- The highest percentage of total O&G loss was measured in LF5 (75%), followed by BR2 (69%) and BR3 (67%).
- The decrease in O&G concentrations in LF5, BR2 and BR3 was due to both weathering and biodegradation; however, most of these losses were due to weathering and not biodegradation.
- The percentage reduction in the n-alkanes in the above three methods follows a similar trend.
- The highest decrease in the n-alkanes was observed in LF5, followed by BR2 and BR3, as can be seen from C17/pristane and C18/phytane ratio plots and the gas chromatographs for these three cells.
- The extent of the biodegradation in LF5 was classified as moderate with a rank of "4", while the extent in BR2 and BR3 was classified as light with a rank of "3".
- The range of moisture contents in BR2 (10.5% to 3.2%) was higher than both LF5 (10.5% to 1.7%) and BR3 (7.5% to 1.7%); however, these ranges were considered sufficient to support microbial activities.
- The range of microbial counts in LF5 (3.9E+05 to 2.3E+10 GAB/g) was lower than in both BR2 (2.1E+07 to 2.3E+12 GAB/g) and BR3 (2.1E+06 to 2.2E+12 GAB/g); however, all these ranges were also above the level required to perform the biodegradation process.

From the above it is clear that the performance of LF5 was superior to BR2 and BR3 and it can be concluded that using the bioreactor method for treating oily sludge is not as effective as the landfarming method in the climatic conditions prevailing in Saudi Arabia.

Chapter 5

Mathematical Modeling and Statistical Analysis

5.1 Introduction

The different degradation processes including weathering and biodegradation that took place in the cells and the parameters that influence these processes were discussed in detail in Chapter 4. In this chapter, the kinetics of the degradation processes in the landfarm cells were studied. Three existing models were applied to assess their applicability to the conditions at the test site and to select the model that gives the most representative degradation rate constant. A new model was also developed to better represent the collected data. Factorial analysis was conducted to examine the contribution of tilling, watering, and nutrients on the degradation processes, and their interaction.

5.2 Kinetic Modeling

Mathematical models are tools that have been used by environmental scientists and engineers to simulate and predict the effectiveness of intrinsic biodegradation (Dragun 1988; Lyman et al. 1992). Since the main objective of this work was to study the kinetics

of the degradation process, existing mathematical models were first used to estimate from the data the time required to achieve the desired degradation levels. The following three models were tested:

- Zero-order kinetics;
- First-order kinetics; and
- Monod kinetics.

These models were selected on the basis of their applicability in other studies, their simplicity, and their popularity.

5.2.1 Zero-order Kinetics

Zero-order kinetics is the least reported model in the literature for such studies; however, it has its own scientific and physical significance that makes it applicable to analytical modeling of the degradation process. Lately this model has been used for the natural attenuation modeling of contaminated groundwater (Wiedemeier 1999; Rifai et al. 2000; Khan and Husain 2001, 2002). Physical degradation processes, such as evaporation and volatilization, are generally independent of the contaminant concentration (Equation 1) and are more dependent on physical parameters such as temperature, wind, and pressure. Since this model has the ability to represent these physical processes, which are dominant in many cells in this study, it was decided to test its applicability.

The zero-order decay rate equation can be written as

$$\frac{dC}{dt} = -k_0 \qquad (1)$$

$$C_t = C_0 - k_0 t \quad (2)$$

where:

C_0 = concentration at initial time t_0

C_t = concentration at time t

k_0 = zero-order rate constant

t = time to degrade

5.2.2 First-order Kinetics

First-order kinetics is one of the most commonly used analytical models for biodegradation (Schlauch and Clark 1992; Viraraghavan and Robbins 1995; Taylor and Viraraghavan, 1999). It is simple, easy to apply, and requires only one parameter (k_1), which can be easily estimated.

The first-order decay rate equation commonly used in analytical models is

$$\frac{dC}{dt} = -k_1 C \quad (3)$$

$$C_t = C_0 e^{-k_1 t} \quad (4)$$

where:

t = time to degrade

C_t = concentration at time t

C_0 = concentration at initial time t_0

k_1 = First-order rate constant

The rate of degradation is proportional to the concentration (Equation 3), which is commonly observed in biological and chemical transformation (degradation).

Odermatt (1997) stated that this model has the following unrealistic assumptions:

1. The model does not take into consideration microbial growth.
2. The model does not consider the effect of the loading rate.
3. The first-order biodegradation process is instantaneous and 100% effective at all times.

However he noted that if this model is used for modeling physical processes, the above assumptions might be justifiable.

5.2.3 Monod Kinetics

The Monod kinetics model is the second most commonly used model for the biodegradation of the contaminants (LaGrega et al. 1994). It is a psydo-model with the potential to simulate the "boom and bust cycle" of a microbial population and the impact of ecological factors on the biodegradation process. This model is appealing because it introduces the influence of a microbial population or biomass into the modeling of intrinsic biodegradation (Odermatt 1997).

The Monod kinetics equation can be written as

$$\frac{dC}{dt} = \mu_{max} \frac{CX}{K_s + C} \qquad (5)$$

where:

μ_{max} = maximum specific growth rate (time^{-1})

C = concentration of contaminant at time t (mass/unit volume)

K_s= half-velocity constant (i.e., contaminant concentration at which the specific growth rate is one-half of μ_{max}) (mass/unit volume)

X = concentration of biomass, (mass/unit volume)

The analytical solution for the above equation is shown in Equation 6, where k is considered constant and is equal to $X\mu_{max}$

$$K_s \ln \frac{C_o}{C_t} + (C_o - C_t) = kt \qquad (6)$$

Under limiting conditions where C>> K_s, Monod Equation 5 transforms to a zero-order kinetics model; however, when C<< K_s, the Monod kinetics Equation 5 transforms to a first-order kinetics model.

5.3 Testing of Kinetics Models

The three models (zero-order, first-order and Monod kinetics) were applied to all nine cells. However, detailed analysis was conducted only on the data from three cells (LF1, LF2 and LF5) for the following reasons:

- LF1 represents the natural attenuation conditions (O&G reduction was 57%).
- LF2 represents independent tilling effect (which gave the highest reduction in the O&G concentration of 76%).

- LF5 represents the combined effect of tilling, watering and nutrients (O&G reduction was 75%).

5.3.1 Kinetics Modeling for LF1

Figure 5.1 shows the plots of the three models (zero-order, first-order and Monod kinetics) with the observed data. It is clear from the figure that this zero-order model gives a better fit to the data (R^2 = 0.84) compared to the first-order model (R^2= 0.81). This observation is supported by the fact that the zero-order model represents the physical process, which is dominant in LF1. The zero-order and Monod models gives approximately the same fit to the data (both had R^2 = 0.84). Table 5.1 lists the three models, their respective parameters, and R^2.

As stated earlier, the Monod model is a psydo-model, which transforms to a zero-order model under limiting conditions. As can be seen from Table 5.1, the value of K_s is negative, which is physically impossible. As a result, Equation 5 transforms to Equation 1, which is a zero-order kinetic model representing physical processes.

From the above, it can be concluded that the zero-order kinetics model is the best of the three models for LF1, which represents natural attenuation conditions (i.e., physical process is dominant).

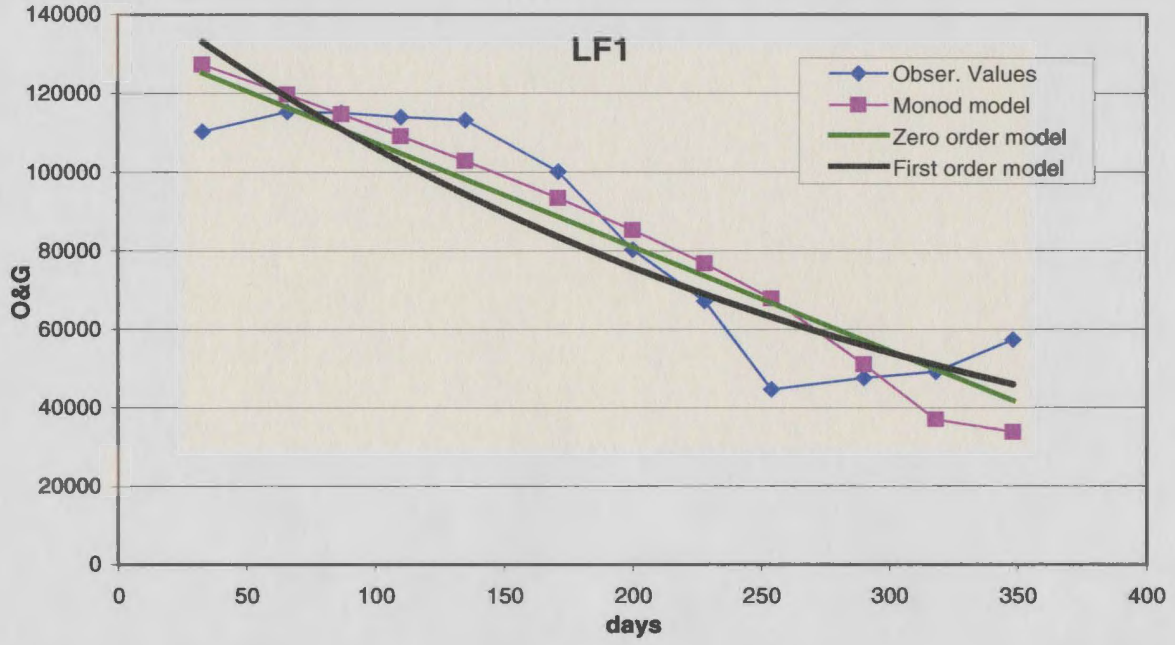

Figure 5.1 Plot of the three models for LF1

Table 5.1 Modeling results for LF1

Model type	Modeled equation	Constants	R^2
Zero-order	C_t= 133835 - 263.91t	k_0=263.91	0.84
First-order	$C_t = 148683e^{-0.0034t}$	k_1= 0.0034	0.81
Monod	dC/dt =157.92C/(-39008+C)	k=157.92 K_s= -39008	0.84

5.3.2 Kinetic Modeling for LF2

Figure 5.2 shows the plots of the three models (zero-order, first-order and Monod kinetics) with the observed data. It is observed from the figure that the zero-order model gave a better fit to the data (R^2= 0.83) compared to the first-order model (R^2= 0.75). This observation is supported by the fact that the zero-order model represents the physical process, which is dominant in LF2. It is also noted that compared to LF1, LF2 has a higher degradation rate. This is mainly due to tilling which caused weathering to become the dominant process in LF2 (Section 4.6.2).

It is also observed from Figure 5.2 that the zero-order model gave a better fit to the data compared to the Monod model (R^2 = 0.81). This indicates that the Monod kinetics model has shifted towards a zero-order kinetics model, which represents the physical process. Table 5.2 lists the three models, their respective parameters, and R^2 values.

From the above, it can be concluded that the zero-order kinetics model is the best of the three models for LF2, where the physical process enhanced by tilling is dominant.

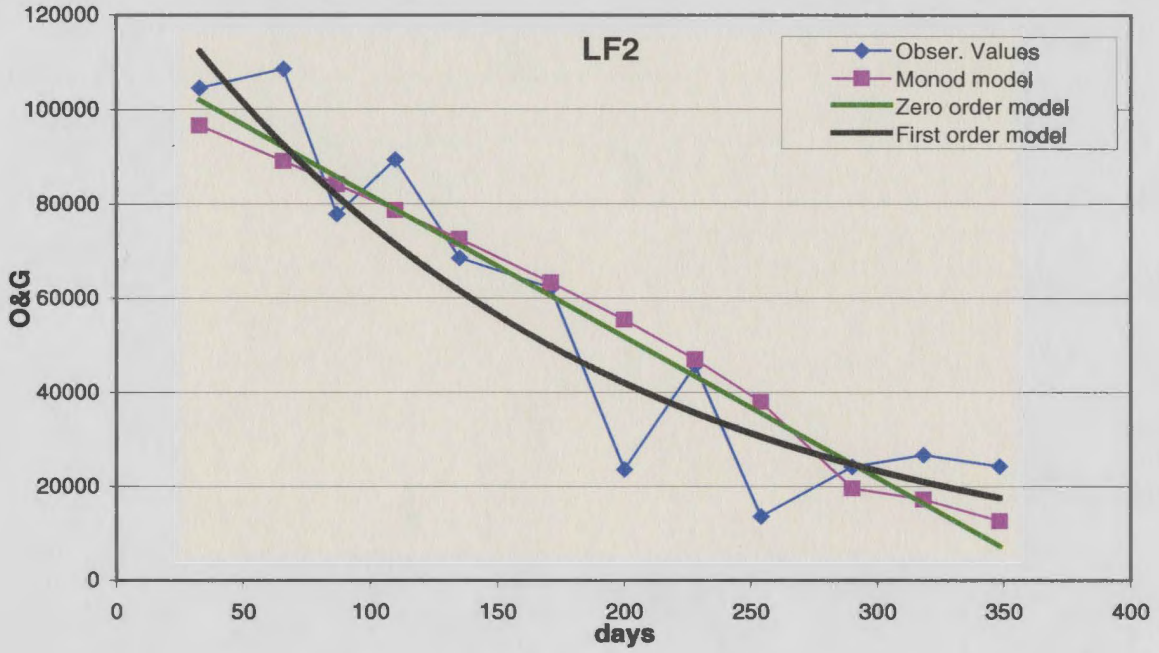

Figure 5.2 Plot of the three models for LF2

Table 5.2 Modeling results for LF2

Model type	Modeled equation	Constants	R^2
Zero-order	$C_t = 111806 - 300.25t$	k_0=300.25	0.83
First-order	$C_t = 136306e^{-0.0059t}$	k_1= 0.0059	0.75
Monod	dC/dt =177.31C/(-20792+C)	k=177.31 K_s= -20792	0.81

5.3.3 Kinetic Modeling for LF5

Figure 5.3 shows the plots of the three models (Zero-order, First-order and Monod Kinetics) with the observed data. It is noted from Figure 5.3 that all three models gave almost the same fit to the data. Monod and the First-order model gave a slightly better fit (R^2= 0.89) compared to the Zero-order model (R^2= 0.88). This observation is supported by the fact that the First-order model represents a concentration-based process that includes biodegradation (Section 4.6.5), apparent in LF5 along with the weathering processes. This has caused a higher biodegradation rate compared to the rates in LF1 and LF2.

It is also observed from Figure 5.3 that the first-order model gave a similar fit to the data compared to the Monod model (R^2 = 0.89). As evident from Table 5.3, the K_s (half-time velocity constant) has a high value (5428), which means that Equation 5 is behaving as a psydo-First-order kinetic model. The higher values of constants (K_s and k) support the observation that biological activities are present in this cell. This is contrary to the observations in LF1 and LF2.

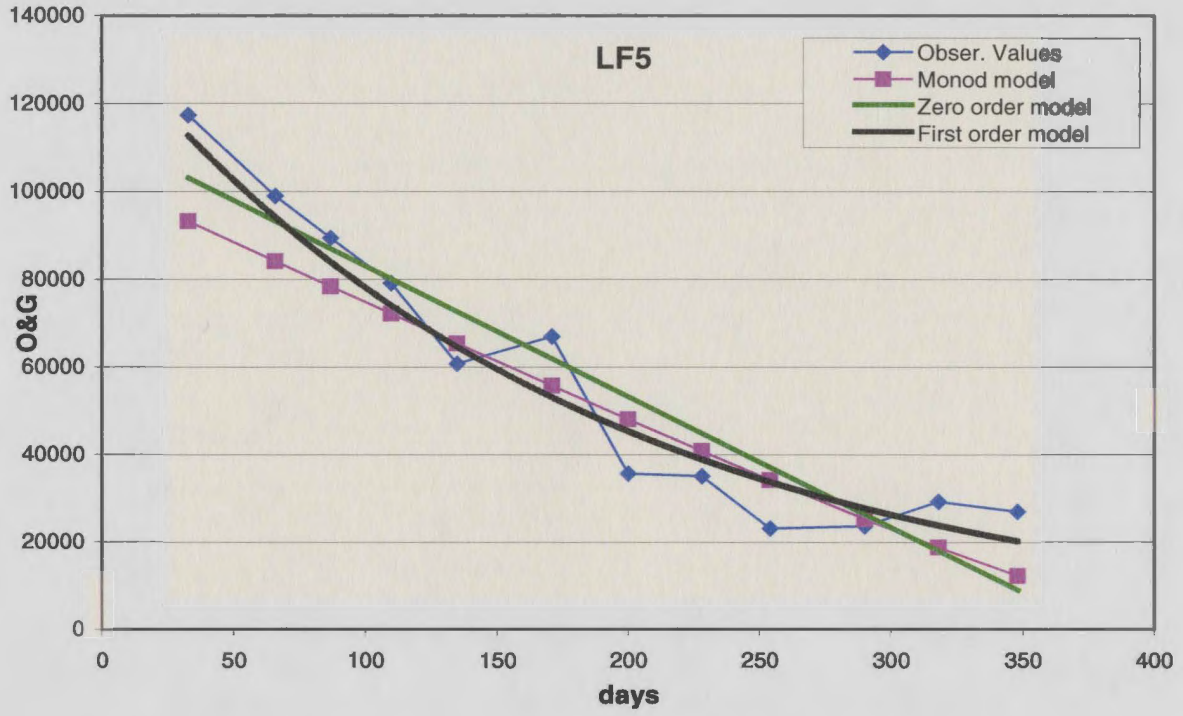

Figure 5.3 Plot of the three models for LF5

Table 5.3 Modeling results for LF5

Model type	Modeled equation	Constants	R^2
Zero-order	$C_t = 112952 - 298.5t$	$k_0 = 298.5$	0.88
First-order	$C_t = 134927e^{-0.0054t}$	$k_1 = 0.0054$	0.89
Monod	$dC/dt = 291.59C/(5428+C)$	$k = 291.59$ $K_s = 5428$	0.89

From the above analysis, it can be concluded that no single kinetics model can represent all the studied cells because most of the available models are designed for laboratory-controlled data, while in field studies conditions such as temperature, pH and microbial types cannot be controlled. In this study, field conditions including temperature and wind (weathering parameters) influenced all degradation process in all of the cells. This has affected the natural biodegradation process and introduced considerable noise (randomness) to the observed data. This has caused further difficulty in developing kinetic models for each cell. Heusemann (1995) similarly concluded that biodegradation models may not be able to predict the biodegradation rate accurately because these are strongly dependent on experimental/field conditions such as temperature, pH, microbial number, and the degree of weathering. He also stated that processes involved in hydrocarbon degradation might change significantly depending upon climatic conditions. It can be further concluded that each cell appears to be better represented by different models (zero- and/or first-order are a better fit for cells where the physical processes are dominant, while Monod fits better for those where biological processes are dominant).

5.4 Statistical Modeling

It was evident from the three tested kinetic models (zero-order, first-order, and Monod) that none of them could represent the observed data accurately. It was also noted from the plotted figures of the individual cells (Section 4.6), that all of the data appear to follow a mirror image of an S-shaped curve. As a result, it was decided to develop a model that

could give a better representation of these data. Since the logistic model (Equation 7) represents an S-shaped curve, the new model (Equation 8), the mirror image of (Equation 7), is given by Equation 8.

$$f(t) = \frac{1}{1 + e^{\frac{t - a}{b}}} \tag{7}$$

$$f(t) = \left[1 - \frac{1}{1 + e^{\frac{t - a}{b}}} \right] \tag{8}$$

Equations 7 and 8 have the dependent variable f(t) ranging from 0 to 1. In order to represent the concentration values in its original unit (C_t), Equation 8 was scaled by D, Min, and time was divided by 10. The equation for the new model is shown below:

$$C_t = \left[1 - \frac{1}{1 + e^{\frac{t - a}{b}}} \right] D + Min \tag{9}$$

The model has four constants: D, Min, a, and b, which can be estimated using non-linear regression, where:

C_t = concentration at time t

t = time, days

a and b = constants

$$D = Max - Min \tag{10}$$

where

Max is the average concentration of the first three observations, mg/kg*

Min is the average concentration of the last three observations, mg/kg*

* The average of the first and last three data were taken to be consistent with the calculation for the total reduction in O&G (see sub-section 4.2.1). The Max value represents the approximate initial value and Min represents an approximate ending value.

The relationship between total reduction and Equation 10 is

$$\text{Totalreduction}(\%) = \frac{D}{\text{Max}} 100 \qquad (11)$$

This new model was applied to all nine cells. However, detailed analysis was conducted on three cells (LF1, LF2, and LF5) for the same reasons that the kinetic models were applied to these cells (see Section 5.2).

Figures 5.4, 5.5 and 5.6 show the plotted data and fitted model obtained from LF1, LF2 and LF5, respectively.

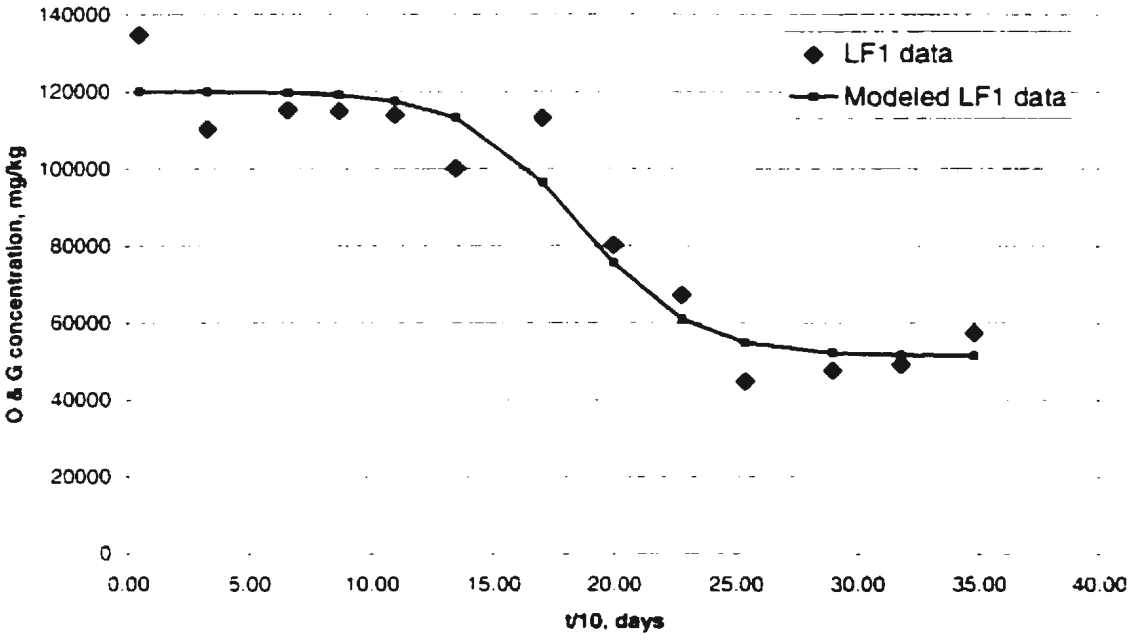

Figure 5.4 Plot showing LF1 data and fitted model

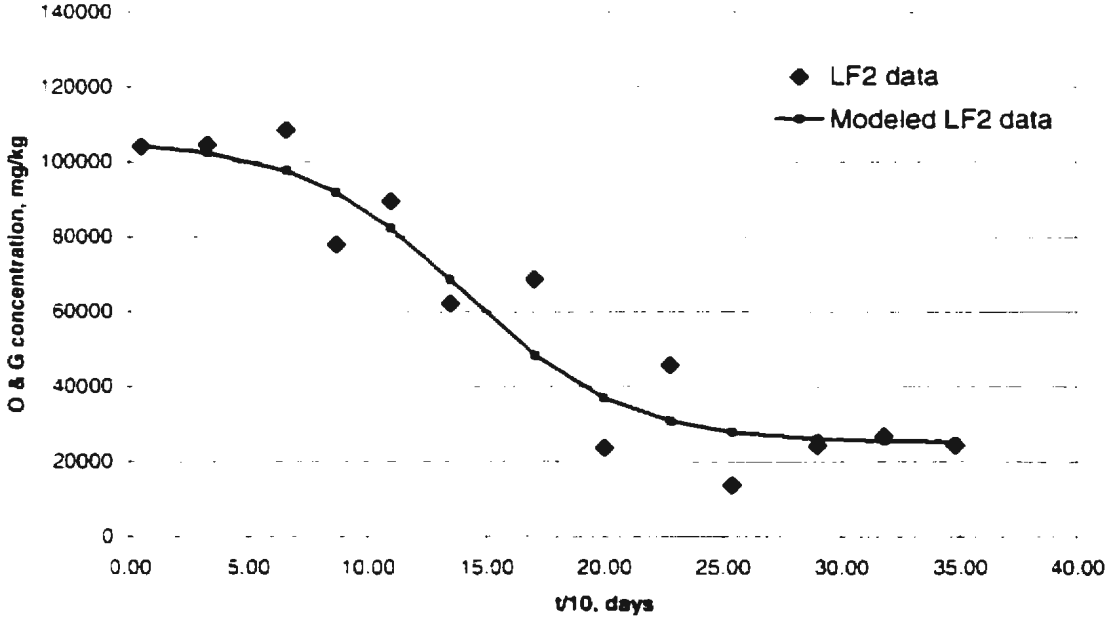

Figure 5.5 Plot showing LF2 data and fitted model

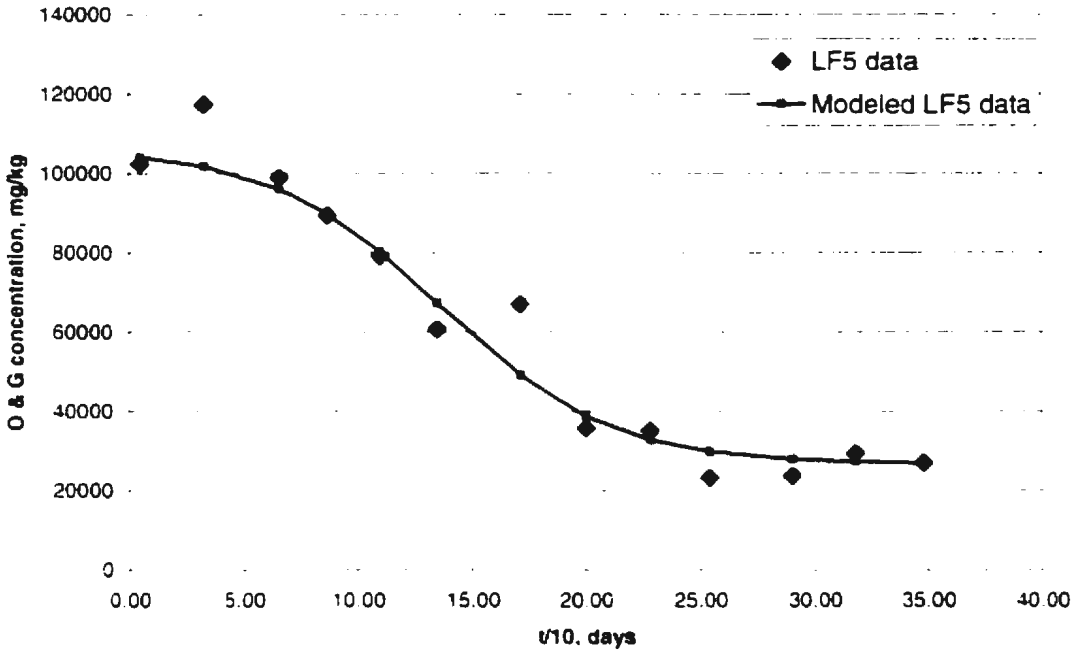

Figure 5.6 Plot showing LF5 data and fitted model

The four constant values (a, b, D and Min) and the R^2 for the three tested cells are presented in Table 5.4.

Table 5.4 Statistical modeling results for LF1, LF2, and LF5

Cells	Values of the parameters used in Equation 9					R^2
	a	b	D	Max	Min	
LF1	18.59	2.31	68636	120118	51482	0.953
LF2	14.02	3.39	80582	105654	25072	0.923
LF5	13.66	3.68	79581	106253	26672	0.951

It is clear from Table 5.4 that all the R^2 are higher than with the three models tested earlier. While analyzing the different curves it was observed that those with higher initial lag phases have higher values of constant "a". It was also observed that the curves with the longer periods of sharp degradation have higher values of constant "b". From these observations, it is believed that constant "a" represents the initial lag phase while constant "b" represents the sharp degradation phase. It is important to emphasize that this interpretation of constants "a" and "b" is tentative at present and needs to be further researched.

5.5 Statistical Analysis

Both LF2 and LF5 gave the highest reduction in the O&G levels among the nine tested cells, although they received different treatment methods (LF2 had tilling only while LF5 had tilling, water, and nutrients). Since the percentage reductions in the O&G in both cells were close (76% for LF2 and 75% for LF5), the analysis of covariance (ANCOVA) was conducted to statistically determine if the degradation rates (slope) and the loading rates (intercept) are significantly different. ANCOVA is based on linear regression with time (days) as the co-variate.

The general regression model used is

$$C = \beta_0 + \beta_1 X + \beta_2 Z + \beta_3 ZX + \varepsilon \qquad (12)$$

where:

C represents concentration in mg/kg

X represents time in days

Z is equal to 0 if data is from LF2 and equal to 1 if data is from LF5

ZX represents an interaction term

A significant value of $\beta 2$ would indicate that the relationship between concentration (C) and time (X) is different for each cell (change is intercept). If a significant value of $\beta 3$ is observed this means that the relationship between concentration (C) and time (X) is different for each cell (change is slope).

The complete test was conducted using Minitab (Minitab 1998), and the results are shown in Table 5.5. From the table it is clear that "P" values for both $\beta 2$ and $\beta 3$ are high (far greater than 0.05), which means that $\beta 2$ and $\beta 3$ does not significantly affect the concentration versus time relation. This implies that LF2 and LF5 data are not significantly different.

Table 5.5 Minitab results for ANCOVA of LF2 and LF5

```
The regression equation is
LF2-5 = 108416 - 293 X + 365 Z + 5.2 ZX

Predictor         Coef        StDev           T        P
Constant        108416         6600       16.43    0.000
X              -292.57        33.23       -8.80    0.000
Z                  365         9334        0.04    0.969
ZX                 5.21        47.00        0.11    0.913

S = 12801       R-Sq = 87.4%     R-Sq(adj) = 85.7%

Analysis of Variance

Source            DF           SS           MS          F        P
Regression         3 25039662497  8346554166      50.78    0.000
Residual Error    22  3616253044   164375138
Total             25 28655915541
```

The fitted models (linear and S-shape) for LF2 and LF5 were plotted (Figures 5.7 and 5.8) to further illustrate that both cells behaved similarly in terms of the reduction of their O&G levels. The trend lines for both cells (in the two models) almost overlapping, indicating that both types of treatments produced the same results.

From this it can be concluded that whether tilling was applied alone or with the addition of water and nutrients, the final reduction in the O&G will be almost the same in arid regions. It should also be noted that biodegradation in LF5 (which is mainly attributed to the addition of nutrient and water) was greater than LF2, however, the contribution of biodegradation was very small as compared to weathering.

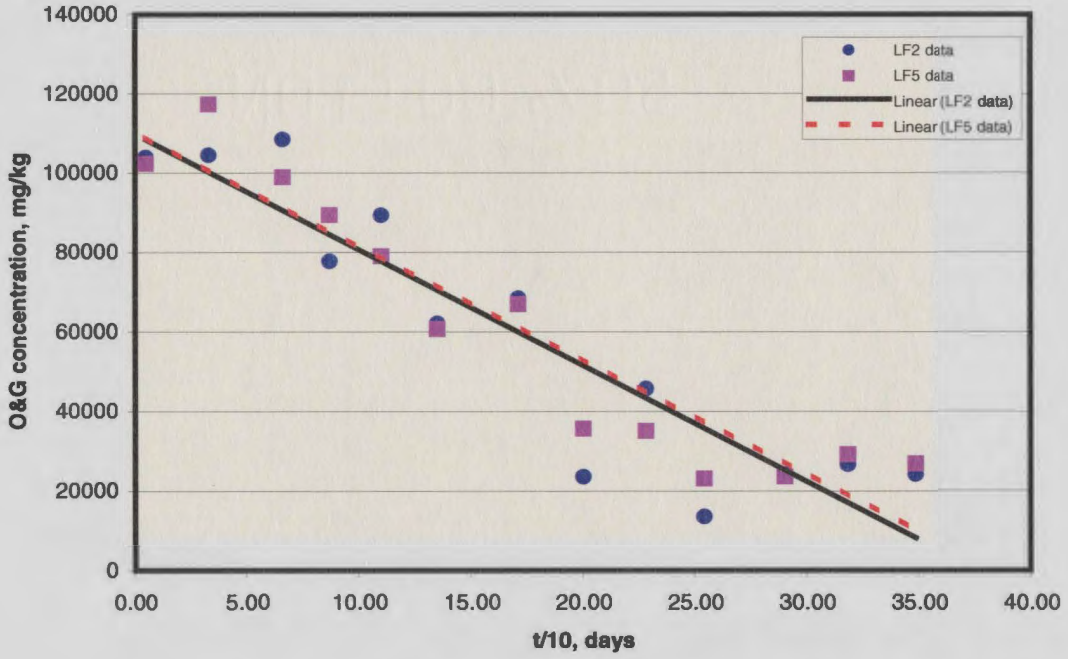

Figure 5.7 Plot showing the fitted linear curves for LF2 and LF5

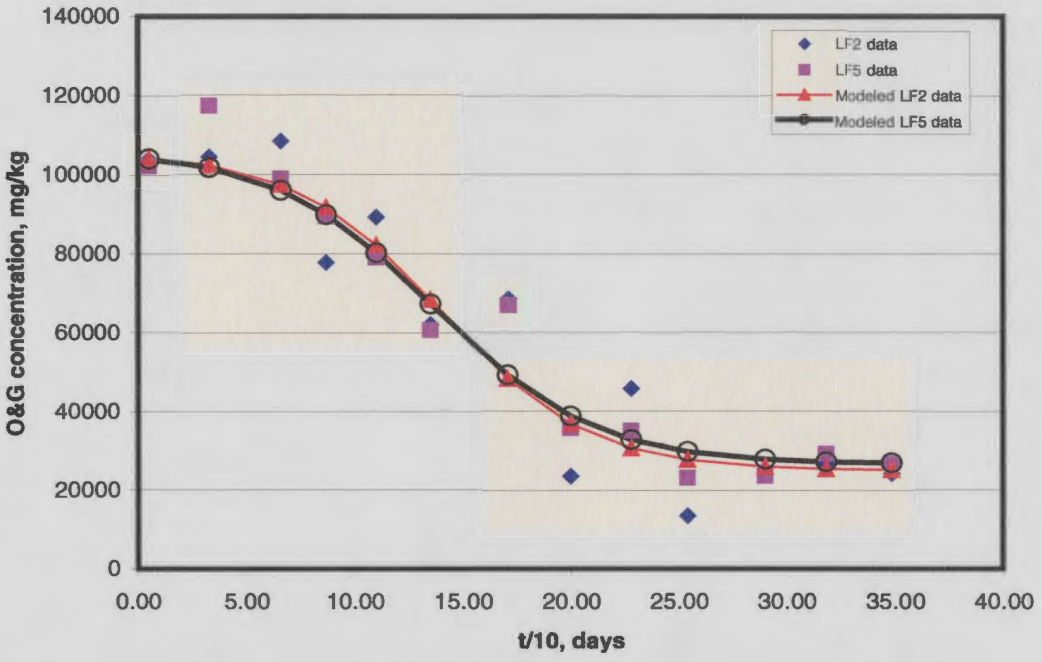

Figure 5.8 Plot showing the fitted mirror image of S-shaped curves for LF2 and LF5

5.6 Two-level Factorial Analysis

The two-level factorial analysis (2^k) was used to evaluate the differences in the performance of four landfarm cells (LF2, LF3, LF4, and LF5). It was also used to determine how each of the operating parameters contributed to the degradation process and the interaction between the parameters. The operating parameters used in this study were tilling, the addition of water, and the addition of nutrients. The common operating parameter that was applied to all these cells was tilling. As mentioned in Section 3.2, only the effect of water and nutrients in the presence of tilling was studied, i.e., the effect of tilling alone (LF2), tilling with water (LF3), tilling with nutrients (LF4), and tilling with water and nutrients (LF5).

Two main responses were studied by total degradation and first-order degradation rate constant methods. The test factors and the response of interest are shown in Table 5.6. The two levels are referred to as low and high levels respectively.

Table 5.6 Test factors and response for the hydrocarbon degradation experiment

Factor	**Name**	**Low Level (-1)**	**High Level (+1)**
A	Water	No Water	Water
B	Nutrients	No Nutrients	Nutrients
Response 1: Total degradation (decrease in O&G concentration after one year, C_T)			
Response 2: First-order degradation rate constant for O&G, 1/day			

For any 2^k experiment, all combinations of the k factors must be considered. With two factors, there will be four treatment combinations. Table 5.7 shows the layout of all combinations.

Table 5.7 Treatment combinations

Run	Combination	A	B	Description of combinations
1	(1)	-1	-1	no water, no nutrients
2	a	+1	-1	water, no nutrients
3	b	-1	+1	no water, nutrients
4	ab	+1	+1	water and nutrients

The symbols used in Table 5.7 under the heading of Combination, are explained below:

"(1)" - all factors are at the low level.

"a" - only factor A is at the high level, all other factors at the low level.

"b" - only factor B is the high level and all other factors at the low level, and

"ab" - both factors are at the high level.

Under the headings of "A" and "B" are the coded values of a and b, and the meanings of the symbols used are as follows:

"+1" - high level

"-1" - low level

Using "+1" and "-1" to indicate the combinations is the preferred method in most software for the design of experiments.

5.6.1 Analysis for Response 1: Total Degradation (%)

The first response that was analyzed by the two-level factorial analysis was the reduction in O&G levels. The decrease was measured in each of the four test cells and the results are shown in Table 5.8. This table was also used to calculate the effect of each factor as well as the interaction of all these factors.

Table 5.8 Factorial design analysis result for total degradation

Combination	A	B	AB	Total degradation (%)	Corresponding cells
(1)	-1	-1	+1	76	LF2
a	+1	-1	-1	71	LF3
b	-1	+1	-1	40	LF4
ab	+1	+1	+1	75	LF5
$\bar{Y}_+$	73.0	57.5	75.5		
$\bar{Y}_-$	58.0	73.5	55.5		
Effect (Δ)	15.0	-16.0	20.0		

The AB column is used to estimate the interaction between A and B. The "+1" and "-1" signs are obtained by multiplying the signs in columns A and B. The equal numbers of positive and negative signs means that the design is orthogonal, which is a desirable property. The effect of factor A is calculated as follows:

Average of (+) responses = (71 + 75)/2 = 73

Average of (-) responses = (76 + 40)/2 = 58

Effect of A or Δ_A = 73 – 58 = 15

Δ_A measures the average change in Y as A changes from a low to a high level.

From the above it can be concluded that the addition of water resulted in an average increase of 15% in O&G level reduction. Similarly, the effects of adding nutrients alone (B) resulted in a negative effect (-16%), which can be interpreted as an average decrease in hydrocarbon concentration reduction. The effect of adding both water and nutrients

together (AB) resulted in a positive effect of 20%. The largest effect is the interaction effect AB of 20 which measures the change in the effect of one factor as another is changed. The equation developed from this analysis is shown below (Equation 13). In view of a large interaction effect, the individual effects are meaningless and the joint effect is the one to be considered.

Total degradation = 65.50+7.5A-8.0B+10AB (13)

Where:

65.50 is the overall mean, the regression coefficients are half the effect size, and A and B are coded values (+1, -1).

Figure 5.9 is a plot showing the interaction between factors A and B. From this figure, it is clear that when both water and nutrients were not added, the best response (reduction in the O&G) of 76% is achieved. When water is alone added, the response achieved is 71%, and when both water and nutrients are added, the response is 75%. Since all treatment combinations were conducted with tilling alone, this clearly indicates that the best reduction in the O&G level is achieved when tilling is applied alone without the addition of either water or nutrients.

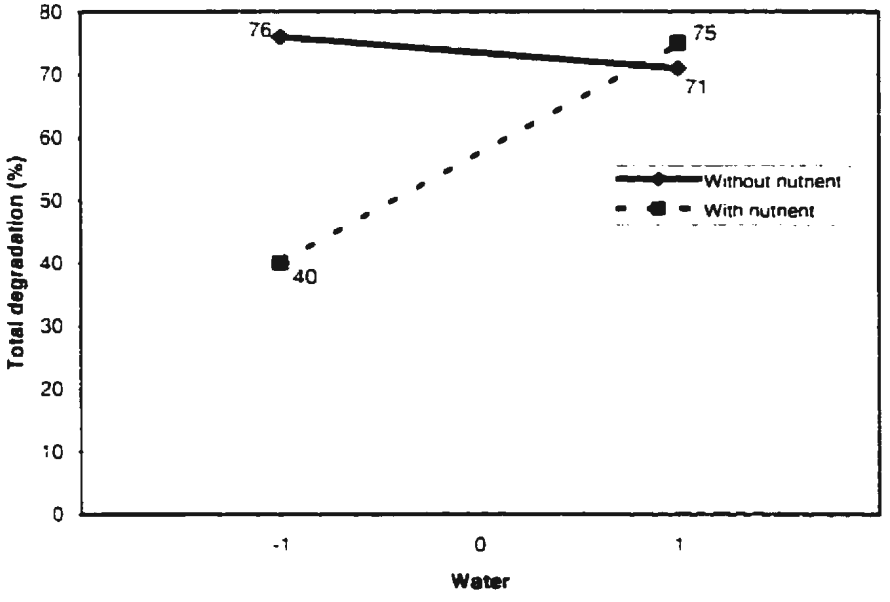

Figure 5.9 Plot showing interaction effect for total degradation

5.6.2 Analysis for Response 2: First-order Degradation Rate Constant (1/day)

This second response that was analyzed by the two-level factorial analysis is the First-order degradation rate constant. This was done to study the effects of the operating parameters on the degradation rate constants. The analysis conducted on this response is similar to that conducted on the first response. The degradation rate constant (1/day) was estimated for First-order kinetics in each of the four test cells and the results are shown in Table 5.9. This table was also used to calculate the effect of each factor as well as the interactions of all these factors.

Table 5.9 Factorial design analysis result for degradation rate constant

Combination	A	B	AB	Degradation rate constant (1/day)	Corresponding cells
(1)	-1	-1	+1	0.0059	LF2
a	+1	-1	-1	0.005	LF3
b	-1	+1	-1	0.0025	LF4
ab	+1	+1	+1	0.0054	LF5
$\overline{Y}_+$	0.0052	0.0039	0.00565		
$\overline{Y}_-$	0.0042	0.00545	0.00375		
Effect (Δ)	0.001	-0.0015	0.0019		

From Table 5.9 it can be observed that the addition of water alone (A) resulted in a positive effect of 0.001, while the addition of nutrient alone (B) resulted in a negative effect of 0.0015 (meaning a decrease in degradation rate constant). The largest effect was also the interaction of water and nutrients (interaction effect of AB), which is 0.0019. The prediction equation developed from this analysis is shown below (Equation 14).

Total degradation = 0.0047+0.0005A-0.00075B+0.00095AB (14)

where 0.0047 is the overall mean, the regression coefficients are half the effect size, and A and B are coded values (+1, -1).

Figure 5.10 is a plot showing the interaction between the two factors A and B. From this figure, it is clear that when tilling was applied in the absence of water and nutrients, the highest degradation rate constant of 0.0059 1/day was achieved. When water was added,

the presence or absence of nutrients gave similar responses (0.0054 versus 0.005 1/day). Since all the treatment combinations were conducted with tilling, this clearly indicates that the highest degradation (loss to atmosphere) rate was achieved when tilling alone was applied without the addition of either water or nutrients.

From the above analysis, it can be concluded that the best operating treatment is tilling alone without the addition of either water or nutrients and that their addition will only increase the operation cost but will not increase the degradation rate or the reduction in O&G levels.

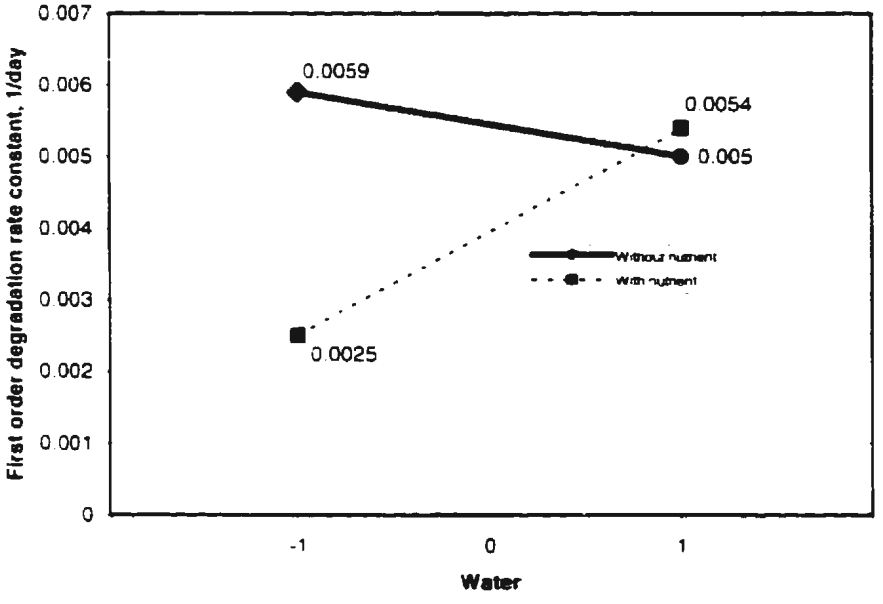

Figure 5.10 Plot showing interaction effect for first-order degradation rate constant

Chapter 6

Risk Assessment

6.1 Introduction

In Chapter 5 mathematical models were applied to determine which model is most applicable to the degradation process that occurred at the tested cells. Statistical analyses were also conducted to evaluate the differences in the performance of the landfarm cells. In this chapter, the health risk associated with a landfarm operation for the onsite workers was assessed.

The risk associated with a landfarm operation is mainly due to the release of hydrocarbon compounds as a result of applying the sludge to the soil and as a result of oily sludge degradation. The people who are directly exposed to these hydrocarbons include those who bring and apply the sludge to the site, workers who operate landfarming equipment such as dozers, and those who routinely collect samples from the landfarms. Figure 6.1 shows a typical sludge application to a landfarm while workers and equipment operators are present. Figure 6.2 shows the operation of a landfarm, with a dozer being used for cultivating the sludge.

Figure 6.1 Oily sludge application to a landfarm

Figure 6.2 Tilling of oily sludge

One of the objectives of this study was to assess the health risk to onsite workers associated with VOC emissions resulting from a landfarm operation. To fulfill this objective, a detailed risk analysis was conducted; in the first approach, values monitored from this study were used; and in the second, mathematically calculated values of contaminant concentration in the environment were used. The complete procedure followed in conducting the risk assessment is presented in Figure 6.3.

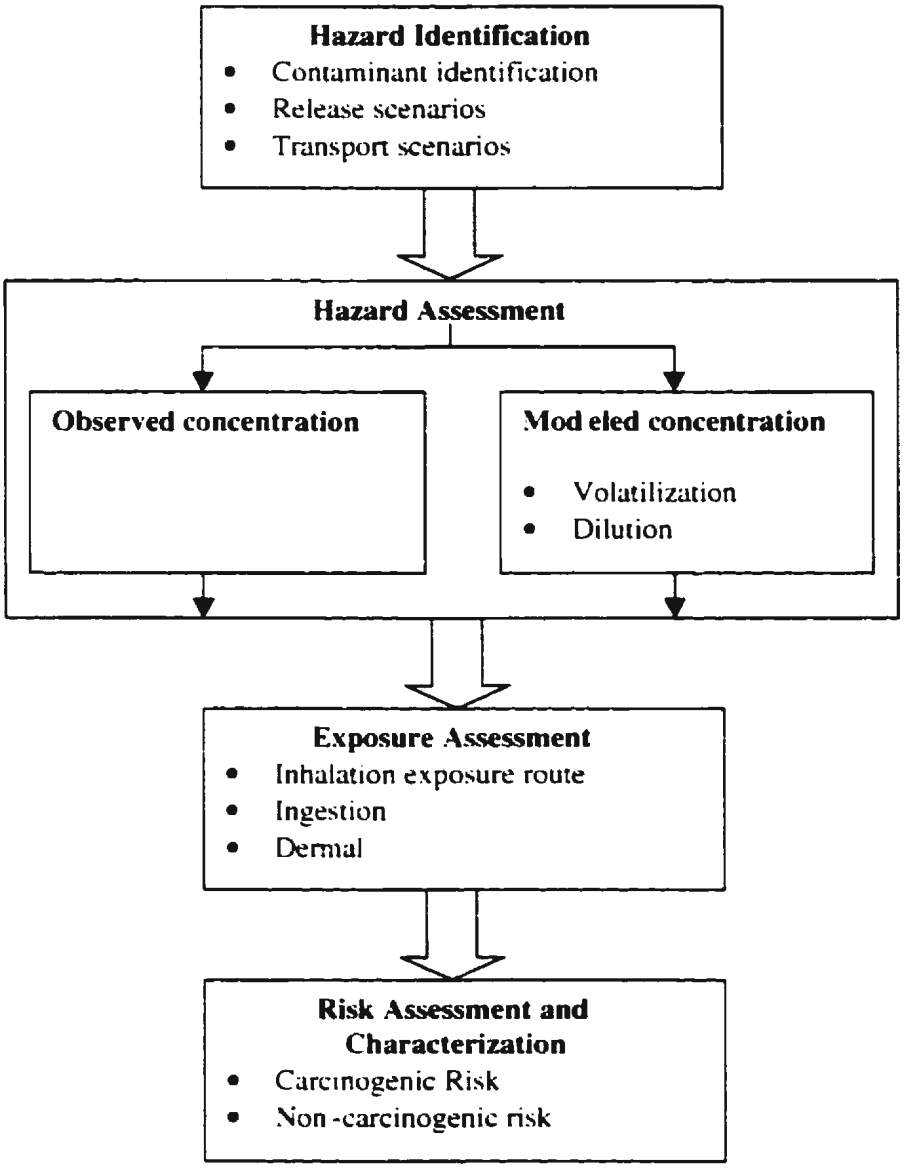

Figure 6.3 Framework of the risk assessment used in the present study

6.2 Hazard Identification

A landfarm can pose many types of hazards to the environment, ecology, and human health through various exposure pathways:

- toxic organic compounds and or heavy metals may leach to the groundwater causing contamination, which on consumption may cause health problems.
- heavy metals and/or organic compounds may migrate through the soil and contaminate other sites.
- light volatile organic compounds may become airborne and come in contact with onsite and or offsite receptors through inhalation and ingestion and cause serious health problems.

Of the three possible scenarios mentioned above, scenarios 1 and 2 are not likely to occur at the studied site because:

1. The groundwater at the present site is more than 6 m below ground surface, and it is unlikely that contaminants from a landfarm will leach to the groundwater. The experimental investigation also shows no leaching of contaminants to the groundwater (see Section 4.2.4).
2. Although it is likely that residual organic compounds and heavy metals may migrate through the soil to other locations, the present site is in a remote area and any possible receptor is located more than 2 km from the site. Therefore, this study does not include any risk assessment to offsite receptors.

The third scenario is the one that is most likely to occur as a result of the high temperature and wind, and cause the volatilization of organic compounds. These compounds would be inhaled by onsite workers or transported to offsite receptors. The

risk assessment reported in this chapter covers the third scenario for onsite workers. The risk agents considered are benzene, toluene, ethylbenzene, and xylene (BTEX).

Oily sludge is comprised of thousands of organic compounds of variant characteristics. It is almost impossible to take account of these compounds individually or in combination. Among these compounds, benzene, toluene, ethylbenzene, and xylene are commonly used for risk assessment because they are readily volatilized, persistent in nature, and are considerably toxic (Covello and Merkhofer 1994; Rifai et. al. 2000; Khan and Husain 2001, 2002). Benzene is a known carcinogen. As per the occupational health and safety administration (OSHA), the allowable 8 hours exposure limit of benzene is 1 *ppm* (Benzene fact sheet, 2001). Toluene is a suspected teratogen and its prolonged exposure may cause liver, kidney and brain damage (Toluene fact sheet, 1998). As per the OSHA, eight hour work exposure should not exceed 200 *ppm* (Toluene fact sheet 1996); Ethylbenzene is suspected to cause mutations and liver damage; eight hours of work exposure should not exceed 100 *ppm* (Ethylbenzene fact sheet 1996). A lengthy exposure to xylene may damage the liver and kidney and affect the normal function of the brain, and 8 hours work exposure should not exceed 100 *ppm* (Xylene fact sheet 1998).

6.3 Hazard Assessment

Two methods were used for the hazard assessment. The first is based on the observed concentration in one of the cells (BR2), and the other is based on the volatilization

potential and subsequent dilution. Volatilization and dilution were calculated using ASTM's (1995) proposed model (Equation 1 and 2), which incorporate dilution using the Box model. The site specific data used in the model is presented in Table 6.1, and the results obtained from both approaches are listed in Table 6.2. From these results it was observed that the monitored values are comparable with the modeled concentrations; however, they are slightly lower than the modeled ones. This is believed to be mainly due to two reasons: i) some of the volatile compounds were lost during the initial mixing, which was conducted away from the cell (BR2) and this was not accounted for in the monitored value, ii) although BR2 was covered with a clay liner, it is expected that some of the volatile compounds were lost through the cracks and other unavoidable openings without being accounted for in the monitored values. It was also observed from both the monitored and the modeled data that for the initial period (first three months) of the study, the concentrations of all four reference compounds were quite high. These compounds included benzene, a known carcinogen.

$$C = C_{w} \frac{2L\rho_{s}}{U_{air}\delta_{air}} \sqrt{\frac{D_{eff} H}{\pi\tau(\theta_{ws} + k_{s}\rho_{s} + H\theta_{as})}} 10^{3} \qquad (1)$$

$$C = C_{w} \frac{L\rho_{s} d}{U_{air}\delta_{air}\tau} 10^{3} \qquad (2)$$

Table 6.1 Input data used in the risk assessment study

Parameters	Values			
Characteristics of the experiment cell				
Length of the cell, cm	200			
Width of the cell, cm	200			
Thickness of the cell, cm	30			
Sludge characteristics				
Density of the soil, g/cm^3	1.80			
Water content in soil, cm^3-water/cm^3-soil	0.05			
Air content in soil, cm^3-air/cm^3-soil	0.33			
Total porosity of the soil, dimensionless	0.35			
Fraction of organic content*, g-carbon/ g-soil	0.01			
Receptor characteristics				
Air inhalation rate (CR), m^3/day	20.16			
Contaminant exposure frequency (EF), days/year	100			
Exposure duration (ED), years	6			
Retention rate of the contaminant (RR), dimensionless	1			
Absorption fraction (ABS), dimensionless	1			
Average body weight of the receptors (BW), kg	60			
Averaging time (AT), days	600			
Contaminant characteristics				
	B	T	E	X
Henry's law constant*, cm^3-water/cm^3-air	0.22	0.26	0.32	0.29
Carbon-water sorption coefficient*, cm^3-water/g-C	4.85	8.41	22.42	10.80
Chemical diffusivity in air*, cm^2/s	0.093	0.085	0.076	0.072
Chemical diffusivity in water*, cm^2/s	1.1E-5	9.4E-6	8.5E-6	8.5E-6
Slope factor**, 1/mg/kg-day	0.029	--	--	--
Reference dose**, mg/kg-day		1.4	0.286	2.0

* Data adopted from ASTM (1995); B stands for benzene, T for toluene, E for ethylbenzene, and X for xylene.

** Values obtained from LaGrega et al. (1994).

Equations 1 and 2 are part of the ASTM proposed models for risk based corrective action guidelines (ASTM 1995). These equations estimate the contaminant volatilization and their subsequent dilution. They were developed based on the conceptual model shown in Figure 6.1. Equation 1 is based on the partitioning of the contaminant from soil and

water to the air and its subsequent dilution in the known volume of air (mixing zone). Equation 2 is simple mass balance of the contaminant from soil and water to the mixing zone. The parameters used in these models are defined in section titled List of Acronyms and Symbols.

Table 6.2 Observed and modeled contaminants concentration in mg/m^3 for BR2

Compounds	9/26/00	10/10/00	11/26/00	12/17/00	2/3/01	3/11/01 & further
Observed concentration in mg/m^3						
Benzene	0.265	0.003	<0.0006	<0.0006	0.0009	<0.0006
Toluene	0.711	0.007	<0.0007	<0.0007	0.0014	<0.0007
Ethylbenzene	0.165	0.001	<0.0008	<0.0008	0.0008	<0.0008
Xylene	0.571	0.005	<0.0008	<0.0008	0.0012	<0.0008
Modeled concentration in mg/m^3						
Benzene	0.350	ND	ND	ND	ND	ND
Toluene	0.776	ND	ND	ND	ND	ND
Ethylbenzene	0.116	ND	ND	ND	ND	ND
Xylene	0.554	ND	ND	ND	ND	ND

ND stands for not detectable

6.4 Exposure Assessment

Receptors – landfarm workers in the present case – would be exposed to airborne contaminants through various exposure routes: inhalation, direct ingestion, and absorption through the skin. A conceptual chart showing possible exposure scenarios is presented in Figure 6.4. Among these possible exposure pathways, inhalation is the most important and dominant one. The risk assessment conducted in this study focused mainly on the onsite workers. It is recommended that in the future, offsite receptors should also be considered.

While calculating the daily contaminant dose using Equation 3, one of the assumptions used was that a landfarm operator works for a total of 100 days a year for six years throughout his life span. For exposure and risk characterization, an attempt has been made to obtain the site-specific data; however, whenever any of these data were not available, the average American adult data available in the literature were used instead (Table 6.1).

$$\text{Daily intake} = C \times CR \times EF \times ED \times RR \times ABS/(BW \times AT) \quad (3)$$

Details of these parameters and their value are shown in Table 6.1. These parameters are also defined in section entitled List of Acronym and Symbols.

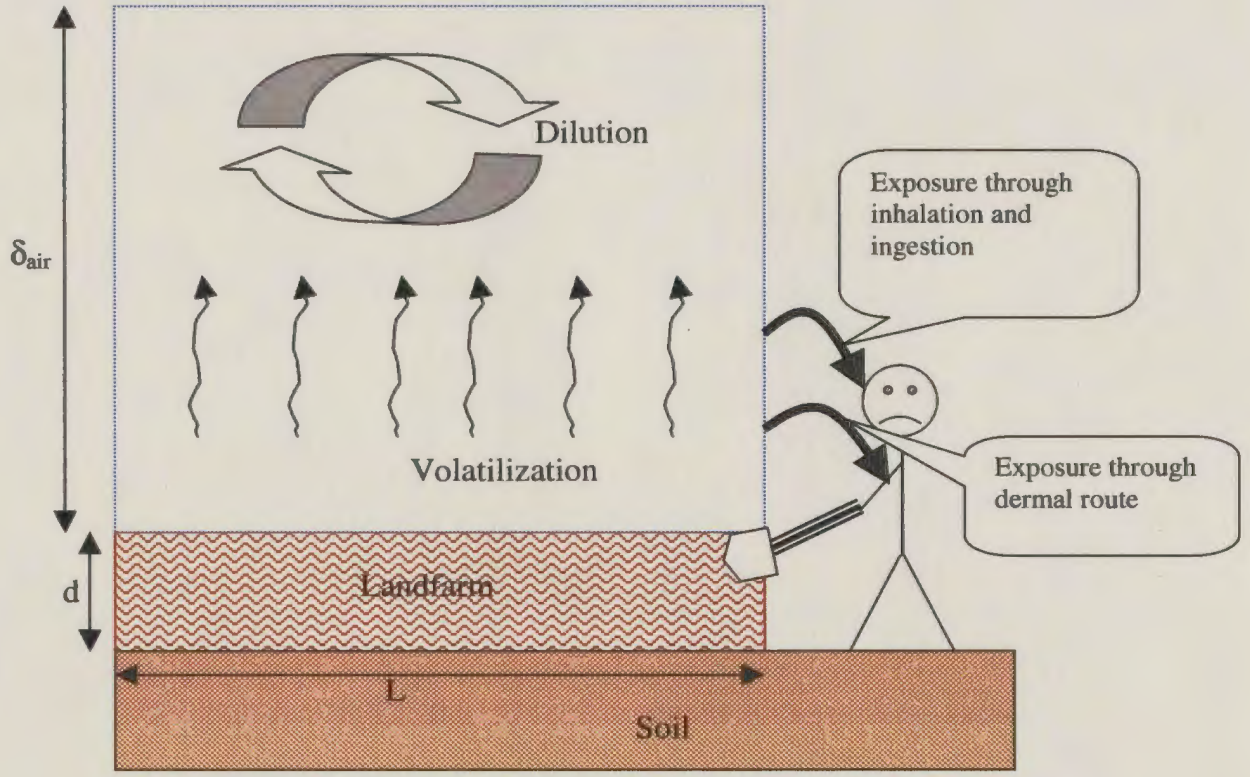

Figure 6.4 Conceptual model of the site and exposure pathways

6.5 Risk Assessment and Characterization

Using observed as well as modeled concentrations, risk factors have been estimated for the inhalation exposure route for all four chemicals (BTEX). Among these four compounds, benzene is a known carcinogen whereas the others are non-carcinogens.

Therefore, both carcinogen (risk factor) and non-carcinogen (hazard quotient) risks were estimated using Equations 4 and 5.

For calculating the risk factor, the slope factor of benzene was used and for calculating the hazard quotient, the referenced doses of toluene, ethylbenzene, and xylene were used. The used values were adapted from LaGrega et al. (1994).

Risk factor = Daily intake x Slope factor (4)

Hazard quotient = Daily intake/Reference dose (5)

The calculated risk factors for both approaches are listed in Table 6.3. From this table it is clear that both approaches (monitored and modeled concentrations) predicted similar results.

The monitored values show that for the first month working in a landfarm, an average worker exposed to a benzene concentration of 0.265 mg/m^3 would have a cancer risk of 2.58E-03. According to the modeled concentration, the calculated risk for the first month is 3.41E-03. These numbers signify that out of 1000 people exposed to this condition 2.58 people are likely to get cancer as per the observed value and 3.41 as per the modeled value. Both values (2.58 and 3.42) are 258 and 341 times higher, respectively, than the acceptable value (1.0E-06). However, as the concentration of benzene depletes in the

following 90 days, the cancer risk to the workers decreases and ultimately reaches the acceptable level of 1.0E-06.

Based on the above, it can be concluded that the first three months of sludge application poses serious carcinogen risk to onsite workers. However, after this period and as most of these compounds evaporate, the detrimental risk of these compounds becomes acceptable.

The conducted risk assessment clearly showed that landfarming at the study site poses detrimental risk through the air pathway (through the inhalation exposure route) to site workers. Since this assessment was conducted on a small cell (2 x 2 m), the obtained results should be extrapolated for any large size landfarms in similar arid and hot regions. The important conclusions drawn from this study include:

- Landfarm activity poses serious onsite risk and may also pose serious offsite risk, particularly at the initial period of the loading. If the loading is on a continuous basis, the initial period may be sustained for a long time.
- Tilling activities will enhance volatilization, and this will further add to the risk potential to field personnel.
- The ASTM's volatilization and dilution model was able to represent the monitored values appropriately. It is believed that this methodology along with the model can be used for the risk assessment of a real landfarm. However, additional models need to be incorporated for offsite transport and exposure.

From the above conclusions, the following recommendations are made:

- To select and design any landfarm, a detailed risk assessment analysis must be conducted to ensure that it does not pose a significant risk to onsite and offsite receptors.
- Safety guidelines must be developed for onsite landfarming activity and must be strictly followed.

Table 6.3 Risk factor for observed and modeled conditions

Date	Observed Risk				Modeled Risk			
	Carcinogenic	Non-carcinogenic			Carcinogenic	Non-carcinogenic		
	B	T	E	X	B	T	E	X
9/26/2000	2.58E-03	<1.0	<1.0	<1.0	3.41E-03	<1.0	<1.0	<1.0
10/10/2000	2.92E-05	<1.0	<1.0	<1.0	<1.0E-06	<1.0	<1.0	<1.0
11/26/2000	≤1.0E-06	<1.0	<1.0	<1.0	<1.0E-06	<1.0	<1.0	<1.0
12/17/2000	≤1.0E-06	<1.0	<1.0	<1.0	<1.0E-06	<1.0	<1.0	<1.0
02/03/2001	8.77E-06	<1.0	<1.0	<1.0	<1.0E-06	<1.0	<1.0	<1.0
03/11/2001	5.85E-06	<1.0	<1.0	<1.0	<1.0E-06	<1.0	<1.0	<1.0
04/09/2001	≤1.0E-06	<1.0	<1.0	<1.0	<1.0E-06	<1.0	<1.0	<1.0
05/07/2001	≤1.0E-06	<1.0	<1.0	<1.0	<1.0E-06	<1.0	<1.0	<1.0
06/02/2001	≤1.0E-06	<1.0	<1.0	<1.0	<1.0E-06	<1.0	<1.0	<1.0
07/08/2001	≤1.0E-06	<1.0	<1.0	<1.0	<1.0E-06	<1.0	<1.0	<1.0
08/05/2001	≤1.0E-06	<1.0	<1.0	<1.0	<1.0E-06	<1.0	<1.0	<1.0

B is for benzene, T is for toluene, E is for ethylbenzene, and X is for xylene

Chapter 7

Conclusions and Recommendations

This chapter is divided into two parts: the first discusses the conclusions, which are based on the results obtained from this study: the second lists recommendations for future research in the area of degradation under arid conditions.

7.1 Conclusions

In this study a field experiment was conducted on the oily sludge generated from a tank bottom in order to: (1) study the kinetics of oily sludge degradation in landfarms and bioreactors under natural and enhanced conditions, (2) evaluate the effectiveness of combining landfarms and bioreactors for accelerating oily waste degradation rates, (3) assess the effect of increasing oily waste loading under arid conditions, (4) determine if biodegradation is the principle mechanism for oily sludge degradation, and (5) assess the health risk associated with VOC emissions, particularly to landfarm onsite workers. Keeping these objectives in view, the study was conducted and the following conclusions are drawn:

1. The 12-month field study results showed that weathering (evaporation) and not biodegradation is the dominant degradation mechanism (loss) occurring in landfarms and bioreactors in the study area. Morgan and Watkinson (1989) stated that the evaporation of crude oil in temperate climates is minimal and that in hotter climates, up to 40% of the crude may evaporate. The results of this study showed that up to 76% of the O&G in the sludge might degrade as a result of weathering. This is double the amount reported by Morgan and Watkinson.

2. Among the three operating parameters (tilling, addition of water, and addition of nutrients), tilling was the main parameter responsible for achieving the highest rate of degradation (loss). This is evident from the analytical results of O&G, which showed that the cell that received tilling alone (LF2) outperformed all other cells in the percentage reduction of O&G concentrations. The addition of nutrients and water resulted in slowing down the rate of degradation; this is mainly attributed to their effect on the soil properties and hence minimizing weathering. This was also proven by the two-level factorial analysis, which clearly showed that the best response (reduction in O&G) is achieved when tilling alone is applied.

3. Nutrients are key parameters for promoting biodegradation. Only the cells where nutrients were applied showed evidence for biodegradation (LF4, LF5, LF8, BR2, and BR3). This was clearly demonstrated by the C_{17}/Pr and C_{18}/Ph ratios obtained

from the GC-FID analysis. Although biodegradation occurred at the cells that received nutrients, the extent of biodegradation was greater at those that had both water and tilling. However, the biodegradation was not extensive since the branched n-alkanes were intact. Maximum biodegradation was achieved at LF5, and according to Peters and Moldowan (1993), this extent can be classified as only moderate with a ranking of 4.

4. The addition of nutrients to the cell in the absence of water resulted in moderate biodegradation, but it caused the soil to become more compacted, and as apparent from LF4, minimized the weathering effect

5. A new analytical method known as Open System Pyrolysis was used for the first time in this study to monitor the degradation of oily sludge. The results obtained with this method showed some similarity to those obtained from the O&G method. Since weathering is the predominant cause of degradation (loss) in arid regions, monitoring the reduction of specific compounds with sophisticated methods such as GC-FID or GC-MS is not required. Weathering mostly affects the removal of the lighter volatile compounds (up to C_{20}); therefore, a rapid method to determine only such compounds is required. The Open System Pyrolysis method has the capability of characterizing hydrocarbon components into three distinct groups (LV, TD and TC), and hence this method has considerable potential to be used for monitoring degradation patterns in arid conditions.

6. The indigenous soil microorganisms were capable of biodegrading the hydrocarbons. Their counts reached high levels during the cold season; however, when the hot season began, these counts dropped, but were all at a level which supported biodegradation at all times. The bacterial population in the cell that received double the loading rate (LF8) was as high as that in the other cells. Bacteria also reached their peak of 2.3E+12 by the end of the cold season. This finding contradicts Arora et al. (1982) who stated that because of the decreased aeration from excessive hydraulic loading the bacteria population was greater in columns that received a low application rate than those which received a high application rate. It appears that regardless of the loading rate, tilling and water were effective in keeping the levels at high counts. The moisture in the sludge was also sufficient to support the microbial activities as seen from BR4 where water was not added.

7. Although an in-depth investigation on the types of bacteria responsible for the biodegradation process was not part of this study, a novel bacterial species known as *Burkholderia glumae* was identified for the first time in Saudi Arabia. Although various species of *Burkholderia* are known for their capability of degrading various hydrocarbons, there is no report on petroleum biodegradation with the particular species of *Burkholderia glumae*.

8. The most commonly used models that simulate and predict the effectiveness of intrinsic biodegradation were unable to properly represent the collected data. This is mainly because these models were developed in laboratories under controlled conditions. A new model was developed to reflect the mirror image of the S-shaped curve of the collected data. The results obtained from this model were compared with those obtained from other tested models (zero-order, first-order and Monod kinetics) and have shown a much better fit (R^2). This model has a greater potential to represent the mechanism of the degradation process that takes place under conditions similar to where the study was conducted. However, this model should be tested under other conditions in arid regions to see if it can give a similar representation of the data.

9. The two-level factorial analysis (2^k) was used for the first time in a landfarming study to evaluate the differences in the performance of the tested cells. By using this method, the contribution of tilling, water, and nutrients was evaluated. The contribution of these operating parameters to the degradation process and the interaction between the parameters was also determined.

10. The bioreactor system was not as effective as the landfarm system for achieving the highest percentage of O&G reduction. The decreases in O&G concentrations in the bioreactor cells (BR2 and BR3) were less than that in landfarm cell LF5, which had a similar treatment. This is mainly due to the method by which air was added. Mechanical aeration, instead of tilling, resulted in smaller reduction in the

O&G levels. When the performance of the two bioreactor cells (BR2 and BR3) was compared, it was also apparent that the cover on BR2 did not make any significant difference in the reduction of O&G levels.

11. Natural attenuation should not be used as an on-going treatment/disposal method for oily sludge mainly because it is a very slow process.

12. Landfarm activities pose serious onsite risk, particularly at the initial period of loading (three months). The presence of compounds such as benzene poses serious carcinogenic risk to onsite workers. As a result of increasing the volatilization process, tilling activities contribute to this risk.

7.2 Recommendations

The following recommendations were drawn from observations, limitations, and problems faced during this study. They intend to provide future direction for research in the area of degradation under arid conditions.

1. This study showed that tilling is the key operating parameter responsible for achieving the highest rate of degradation (loss). More research is needed to investigate the method, frequency and depth of tilling.

2. The results obtained from the Open System Pyrolysis and the routine O&G method show some similarities between both methods; however, more work is

needed to establish a useful correlation. If the additional work draws a definite conclusion on the applicability of the Open System Pyrolysis to be used for monitoring O&G degradation, this could mean that the routine O&G method can be replaced by this new method, which is timesaving and environment friendly.

3. The risk analysis showed that the initial period of sludge application poses a serious health risk to onsite workers. This was based on an analysis of BTEX compounds only. Since petroleum hydrocarbon contains other toxic compounds such as PNA, more studies are needed to determine the effect of these compounds individually as well as the combined effect of all known toxic compounds. The impact of landfarming operations on other receptors and the safest distance for the location of landfarm from these receptors also needs to be determined.

4. The developed mirror image for an S-shaped model for this study needs further testing, and its applicability and its constants need verification, and further interpretation. Since this model was developed for a specified duration (fall to fall), it needs to be tested under a different time frame.

5. Dibble and Bartha (1979) stated that the biodegradation of higher aromatic and asphaltic compounds through co-metabolism is dependent on the continued presence of saturate compounds. Since all the hydrocarbons in the cells appear to reach a plateau, a study to determine the effect of second load on the same cell will be needed. This second load will also be used to see if a second S-shaped

curve will occur, and if so, the developed mirror image S-shaped model can be tested against it.

6. There is a need to conduct a thorough study on the newly identified bacterial species, *Burkholderia glumae*, in order to determine its characteristics and applicability in degrading various petroleum hydrocarbon compounds.

7. It is recommended to investigate the relative contribution of hydrocarbon volatilization versus biodegradation in more detail.

Chapter 8

Statement of Originality

The originality and scientific contributions of this study are as follows:

1. The data on mechanism of degradation and degradation rates reported in the literature are mainly based on laboratory work with few studies conducted in the field. This is the first comprehensive field study on landfarming conducted under arid conditions to establish the rate and mechanism of the degradation of crude bottom oily sludge.

2. The mechanisms by which oily sludge degrades under arid and hot climatic conditions were found to be different from the information reported in the literature. In the past most of the work conducted to determine the degradation mechanism of oil sludge emphasized the biodegradation mechanism. This study clearly showed that weathering and not biodegradation was the dominant degradation mechanism in arid conditions where the heat plays a key role in this

process. This study identified that tilling was the dominant operating factor (treatment) in the landfarming operation in arid regions and that the addition of water and nutrients to enhance the degradation process was not so effective. This is the first time that such a finding has been clearly stated. This will result in a change in the operating procedures at landfarms under arid conditions.

3. The mechanism of oily sludge degradation using bioreactor methodology and its performance evaluation with landfarming under field conditions has not been studied before. This study is an attempt to compare the degradation process by the two methods.

4. Although several studies have been conducted in the past to assess the health risk associated with VOC emissions from crude oil and its products, no specific studies assessed the health risk associated with the VOC emissions resulting from landfarm operations. In this study, an attempt was made to assess the effects of VOC emissions from landfarming to onsite workers under arid conditions. The preliminary findings reported in this research show that more in-depth investigations are required to assess the effect of these emissions on workers and offsite receptors.

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Appendix A

Detailed Analytical Procedures

Oil & Grease: EPA 9017A (1998) gravimetric method was used for the analysis of Oil & Grease in sludge where 10 g of the sludge was Soxhlet extracted with Freon 113 for 4 hours. The solvent was removed from the extract using a Zymark Turbo Vap Concentrator and the oil and grease measured gravimetrically. The oil and grease was determined as follows: 10 g of wet sludge was weighed in a 150 ml beaker and 10 g of anhydrous sodium sulfate was added to the beaker. The mixture was mixed thoroughly and left to stand for 10 minutes, and then added to the paper extraction thimble. The beaker was rinsed with Freon and added to the thimble. It was then extracted in Soxhlet apparatus for 4 hours using 200 ml of Freon. Using filter paper (Whatmann #2), the extract was filtered into a pre-weighed Zymark tube and the flask and filter paper were rinsed with solvent. The solvent was removed by placing the tube in a Turbo Vap concentrator for about 90 minutes. After the Zymark tube was taken out of the concentrator, it was allowed to come to room temperature (about 30 minutes) and then weighed. The tube was returned to the concentrator for 10 minutes and the same steps were repeated. The final weight was taken and the oil & grease was calculated as follows:

$$\text{Oil \& Grease (mg/kg)} = \frac{\text{weight of oil (mg)} \times 1000\ \text{(g/kg)}}{\text{weight of wet solid (g)}}$$

Total Hydrocarbon (TH): Proprietary pyrolytic methods developed by the Saudi Aramco Research and Development Center were applied to determine total hydrocarbons in the sludge. These methods are related to the application of the Pyrolytic Oil-Productivity Index (POPI; Jones and Tobey 1999; US Patent Number 5,866,814), utilizing the parameters light volatile (LV), thermally distillable (TD), and thermally crackable (TC) hydrocarbons. The analytical method used to determine the presence of hydrocarbons is known as open-system pyrolysis, in which a temperature-programmed instrument heats a small amount of a ground rock sample (sample size was 100 mg; however, to ensure homogeneity of samples, approximately 20 g of sample were ground to a fine powder, and an aliquot of 100 mg was analyzed) from a starting temperature of 210°C (held for 3 minutes) to 600°C at 25 °C per minute. During the heating program, the hydrocarbons driven from the sample are recorded as a function of temperature. Figure A shows a typical instrument output plot (known as a "pyrogram"). A typical analysis results in three peaks. The first is composed of hydrocarbons that can be volatilized, desorbed, and detected at or below 210°C while the temperature is held constant for the first 3 minutes of the procedure. These are called light volatile hydrocarbons (LV). The next phase of pyrolysis consists of a programmed temperature increase from 210°C to 600°C that results in two more distinct peaks. The first of these occurs between ~210°C and ~400°C, and corresponds to thermal desorption of solvent extractable bitumen, or the

light oil fraction. These are called thermally distilled hydrocarbons (TD). The second peak (third peak overall) occurs after about 400°C, generally after a minimum in pyrolytic yield is observed (the temperature corresponding to the minimum in pyrolytic yield is referred to as T_{min}) and extends typically to about 600°C. This peak is due to the pyrolysis (cracking) of heavier hydrocarbons, or asphaltenes. The materials that thermally crack are called thermally cracked hydrocarbons or "pyrolyzables" (TC).

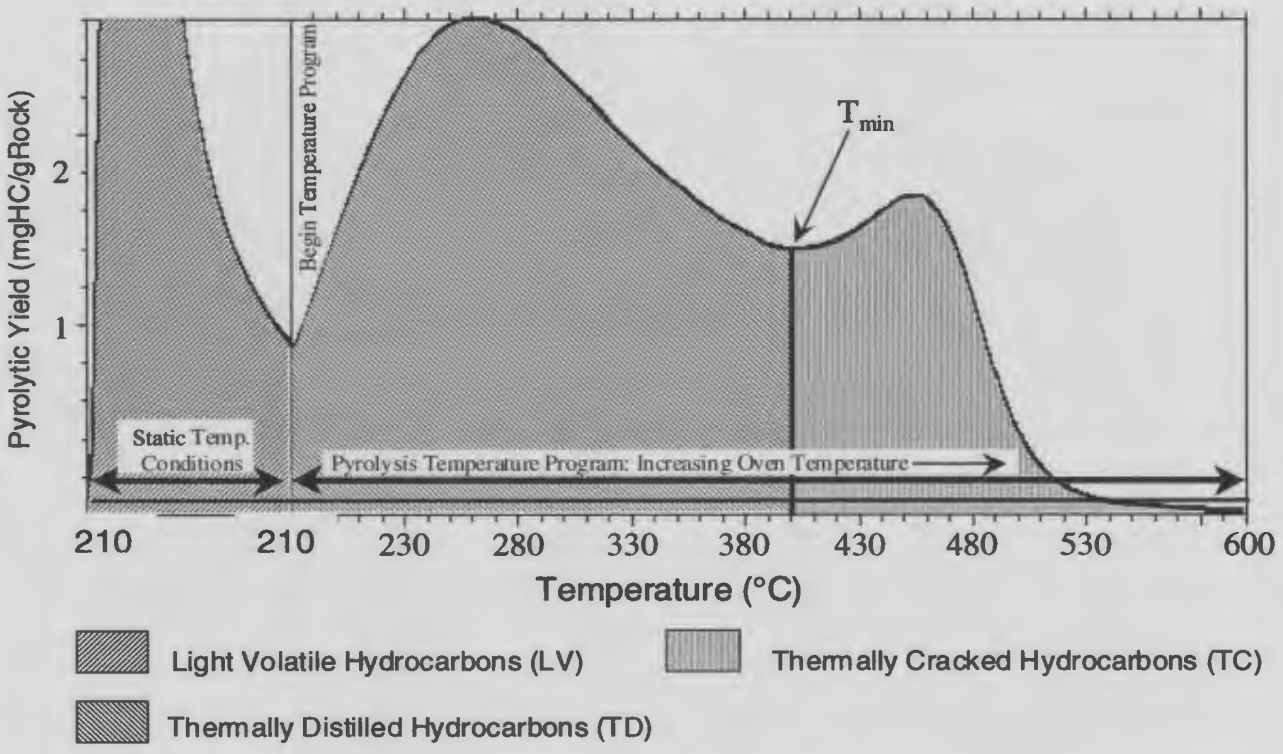


Figure A. Typical output pyrogram from instrument performing open-system temperature programmed pyrolysis (Jones and Tobey, 1999)

Microorganisms: Soil and sludge samples were analyzed for total aerobic bacteria using a triplicate serial dilution method in accordance with method ASTM-D993-58 (1978). One gram of soil (wet) was placed in tubes containing 9 ml of sterile saline solution, and sonicated for 90 seconds to form a cell suspension. The suspension was transferred to growth medium vials for microbial enumerations. The moisture content of each sample was determined concurrently in order to normalize all counts to a one-gram dry weight basis. The results are expressed as MPN (most probable number) per g dry soil.

pH: The determination of pH based on EPA 9045 (1987) where 5 g of sludge sample was placed in a 250 ml beaker and 96.5 ml of distilled water was added to it. The beaker was then covered with a watch glass and stirred vigorously for 5 minutes using a magnetic stirrer. The pH was measure and recorded using a Corning pH meter.

Moisture Content %: The percentage moisture content of soil/sludge samples was determined according to ASTM-D 2216-98 (1998): 2 g of the sludge was weighed into a tared watch glass and dried in an oven at 105 °C for 24 hours. The content was allowed to cool in a desiccator and was weighed. The percentage moisture contents were calculated as follows:

$$\%\ \text{moisture content} = \frac{(\text{grams of sample} - \text{grams of dry sample}) \times 100}{\text{grams of sample}}$$

Total Kjeldhal Nitrogen (TKN): ASTM-D 3590-89 (1995) method was used for the analysis of TKN. The TKN in the samples was determined as follows: 2 g of the sludge was transferred into a 800-ml capacity Kjeldhal flask. One packet of Kel-Pac digestion powder (this ready-to-use powder, consisting of a mixture of potassium sulfate and mercuric sulfate, replaces the digestion solution), 20 ml concentrated sulfuric acid, and two three pieces of boiling stones to prevent bumping were added to the falsk. The mixture was digested in the Kjeldhal flask until sulfur trioxide (SO_3) fumes were given off and heating continued for an additional half an hour. The solution was cooled and diluted with water to about 300 ml and then alkalized by the careful addition of the sodium hydroxide-sodium thiosulfate mixture. The Kjeldhal flask was connected to the condenser, of which the tip is immersed in 2% boric acid solution and was distilled until about 300 ml distillate was collected. A few drops of mixed indicator (mixture of methyl red and methylene blue) were added to the distillate and titrated against 0.02 N sulfuric acid. TKN was calculated as follows:

$$\text{TKN} = \frac{\text{volume of 0.02 N sulfuric acid in ml} \times 280}{\text{sample weight in grams}}$$

Soil Texture: The method, based on ASTM C 136 – 01 (2001), covers the determination of the particle size distribution of fine and coarse aggregates by sieving or screening. The testing procedure was conducted as follows: the sample was dried in an oven to a constant weight at a temperature of 230 ± 9 °F (110 ± 5 °C). The sieves were nested in

order of decreasing size of opening from top to bottom and the sample was placed on the top sieve. The sieves were agitated using a mechanical apparatus for a sufficient period. When sieving was completed, the weight of each size increment was determined by weighing on a balance and the percentages calculated on the basis of the total weight of the sample.

Benzene, Toluene, Ethyl Benzene and Xylene: EPA TO-14 (1988) method was used for the analysis of the air samples, using a Solid Phase Micro Extraction (SPME) sample processing technique. Analytical gas standards were prepared using a volumetric injection of BTEX liquid standard into a 1-L glass sample bulb. The bulb was then heated to 100 °C in an oven for 10 minutes and then cooled to room temperature. The standard was exposed to a 100-µm film thickness poly (dimethylsiloxane) coated fiber for 36 minutes for adsorption of the BTEX compounds. At the end of the adsorption period, the fiber was removed from the gas standard bulb and inserted into the GC injector for GC-MS analysis. The air samples were collected in 6-L Summa-treated stainless steel canisters under atmospheric pressure. These air samples were analyzed by the same procedure used for gas standards.

Benzene in Sludge: EPA 8260 (1998) method protocol was used in the analysis of benzene in the sludge. The analysis was conducted as follows: 4 g of the sludge sample were weighed in a 15-ml vial. 10-ml of methanol were added to the vial, capped and shaken for 2 minutes. 200 µl of the extract and 10µl of internal and recovery standard (5

μg/ml) were added to 10-ml of water in a syringe. The contents of the syringe were transferred to a 10-ml Solid Phase Micron Extraction (SPME) vial, sealed and analyzed for BTEX compounds by SPME-GC-MS.

N-alkanes: The n-alkanes analysis was conducted according to SALAM 340-01 (2001) method. The gas chromatographic analysis of sludge samples were carried out using an Agilent 6890 gas chromatograph with a 30 m x 0.53 mm x 0.88 mm HP-1 column, flow control at 3.2 ml/min He, oven programming from 35 °C to 315°C at 3°C/min and flame ionization detection. Samples were dissolved in methylene chloride and auto-injected using an injection volume of 0.2 μl, an injector temperature of 300°C, and a split ratio of 100:1. The oily material was extracted from the soil samples using a Pressure Flow Extraction apparatus. The organic solvent (MAC solvent) was prepared by mixing Methanol, Acetone, and Chloroform (15:15:70). The soluble organic material recovered from the extraction procedure was then submitted for deasphaltening to remove the asphaltene fraction (SALAM 340-02). Excess n-pentane was added to the sample to precipitate asphaletene, which is insoluble in n-pentane. The maltene (asphaltene-free fraction) was then separated into the saturate, aromatic and resin fractions by HPLC. All fractions were then evaporated to remove the solvent and weighed to determine the weight percentage of each SARA fraction.

Metals: Trace metal analysis in the sludge was determined according to EPA method 6020A (1998) using an Elan 6100 ICP-MS system. The sludge samples were acid-

digested according to US EPA method 3050B (acid digestion of sediments, sludge and soils). About 1 g (dry weight) of sample was digested with repeated additions of nitric acid and hydrogen peroxide. The following metals were determined in the sludge: Ca, Mg, P, K, As, Ba, Cd, Cr, Cu, Pb, Mn, Se, Ag, Ni, V, and Zn.

Appendix B

Water Holding Capacity

SOIL WATER-HOLDING CAPACITY TEST PROCEDURE

1. Clean four 1000 ml separatory funnels. Label them as follows:
   sludge (LF2) 70°C
   sludge (LF2) 110°C
   sand 70°C
   sand 110°C
2. Fit glass wool into the separatory funnels to hold the soil samples and also to filter the drained water.
3. Weigh 800g of sludge (LF2) into each of the separatory funnels labeled as:
   sludge (LF2) 70°C
   sludge (LF2) 110°C
4. Weigh 800g of sand into each of the separatory funnels labeled as:
   sand 70°C
   sand 110°C
5. Add 250ml of water into each of the four separatory funnels, and place funnels on shaker.
6. Drain the water from each funnel into 4 different measuring cylinders and note the time required to drain the first droplet.
7. Remove the stopper and cover (loosely) the mouth of each separating funnel with Aluminum foil.
8. Collect the drained water from each of the funnels and note the volume of the water drained. Calculate the volume of water retained.
9. Set up to two ovens at 70°C and 110°C respectively.
10. Weigh 2g of solid sample from each of the funnels into a weighed watch glass and label them.

10. Place the sludge and sand samples labeled: sludge (LF2) 70°C and sand 70°C in the oven maintained at 70°C for 48 hours.
11. Place the sludge and sand samples labeled: sludge (LF2) 110°C and sand 110°C in the oven maintained at 110°C for 24 hours.
12. At the end of the drying period remove the samples from the oven and place them in desiccators for 30 minutes.
13. Take the weight of the dried samples.
14. Calculated the soil water-holding capacity using the formula:

Soil water-holding capacity (%) = (Water lost / Sample after drying) x100

Trail #1

Temperature: 110°C, Time: 24 hours

Sample	Evap. dish	Sample & dish	Sample	Sample & dish after drying	Sample after drying	Water lost	Soil water-holding capacity
ID	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (%)
LF2-1	28.96	30.95	1.99	30.84	1.88	0.11	05.9
LF2-2	29.09	31.10	2.01	30.99	1.90	0.11	05.8
Sand-1	58.01	60.02	2.01	59.73	1.72	0.29	16.9
Sand-2	57.76	59.76	2.00	59.47	1.71	0.29	16.9

Temperature: 70°C, Time: 48 hours

Sample	Evap. dish	Sample & dish	Sample	Sample & dish after drying	Sample after drying	Water lost	Soil water-holding capacity
ID	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (%)
LF2-1	28.83	30.83	2.00	30.73	1.9	0.1	05.3
LF2-2	32.29	34.29	2.00	34.15	1.86	0.14	07.5
Sand-1	57.77	59.79	2.02	59.48	1.71	0.31	18.1
Sand-2	57.92	59.94	2.02	59.67	1.75	0.27	15.4

Trail #2

Temperature: 110°C, Time: 24 hours

Sample	Evap. dish	Sample & dish	Sample	Sample & dish after drying	Sample after drying	Water lost	Soil water-holding capacity
ID	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (%)
LF2-1	32.31	34.32	2.01	34.24	1.93	0.08	04.1
LF2-2	28.84	30.86	2.01	30.77	1.93	0.09	04.6
Sand-1	57.79	59.77	1.98	59.47	1.68	0.3	17.8
Sand-2	57.92	59.92	2	59.67	1.75	0.25	14.3

Temperature: 70°C, Time: 48 hours

Sample	Evap. dish	Sample & dish	Sample	Sample & dish after drying	Sample after drying	Water lost	Soil water-holding capacity
ID	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (%)
LF2-1	85.97	87.99	2.02	87.88	1.91	0.11	05.8
LF2-2	37.65	39.69	2.04	39.59	1.94	0.10	05.2
Sand-1	84.76	86.76	2	86.50	1.74	0.26	14.9
Sand-2	85.86	87.89	2.03	87.59	1.73	0.30	17.3

Moisture Content Procedure

This test was conducted to determine if the moisture content procedure conducted, measured only water or it measured some volatile hydrocarbons with the water.

Method

- Add approximately 2g sludge samples to four previously weighed evaporation dishes.
- Add known weight of water to two of the sludge samples.
- Place the two types of samples (sludge with water) at 70°C for 48 hrs and the other two at 110°C for 24hrs.
- After drying in the oven, place the samples in a desiccator for 2 hours to cool
- Weigh the samples and evaporating dishes. Determine weight loss of samples
- Calculate the moisture contents of the samples using the formula:

  Moisture content % = (Sample weight after drying /Original sample weight) X 100

Trial #1

Temperature: 110°C, Time: 24 hours

Sample	Evap. dish	Sample & dish	Sample, dish and water	Sample	Water added	Sample & dish after drying	Water lost	Moisture content
ID	Weight (gm)	Weight (gm)	Weight (gm	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (%)
Sludge-1	84.75	86.76	--	2.01	--	86.76	0	0
Sludge-2	37.65	39.65	--	2.15	--	39.63	0.02	0.93
Sludge-1 & H2O	85.96	87.89	88.40	1.93	0.51	87.97	0.43	17.63
Sludge-2 + H2O	85.88	87.89	88.42	2.01	0.53	87.86	0.56	22.05

Trial #2

Temperature: 70°C, Time: 48 hours

Sample	Evap. dish	Sample & dish	Sample, dish and water	Sample	Water added	Sample & dish after drying	Water lost	Moisture content
ID	Weight (gm)	Weight (gm)	Weight (gm	Weight (gm)	Weight (gm)	Weight (gm)	Weight (gm)	Weight (%)
Sludge-1	58.03	60.04	--	2.01	--	60.01	0.03	1.45
Sludge-2	57.78	59.76	--	1.98	--	59.76	0	0
Sludge-1 & H2O	29.09	31.09	31.35	2.00	0.26	31.06	0.29	12.83
Sludge-2 & H2O	28.94	30.96	31.22	2.02	0.26	30.93	0.29	12.72

All sludge samples are from cell # LF2.

Appendix C

Bacterial Identification Results

BIOLOG Solutions in Microbiology

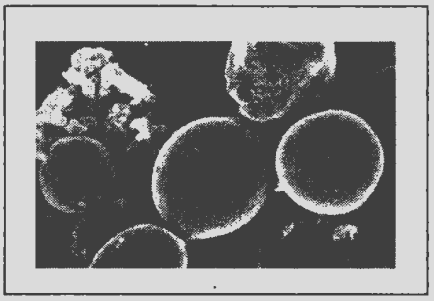
Bacterial Identification Result

Sample Information:

Sample location: Juaymah LANDFARM (LF5)
Under the Project No. ARI 660-01-100
Requester: Ramzi Hejazi
Customer ID# 744-640

Result:

Species ID: **BURKHOLDERIA GLUMAE**



BIOLOG Information

Gram Negative
Aerobes
Growth Temperature = 30°C
Streptococcus

General Information

No information available.

AMZ

Bacterial Identification Result

Sample Information:

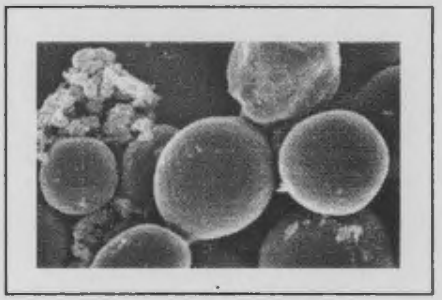
Sample location: Juaymah LANDFARM (LF2)
Under the Project No. ARI 660-01-100
Requester: Ramzi Hejazi
Customer ID# 744-640

Result:

Species ID: **BURKHOLDERIA GLUMAE**

BIOLOG Information

Gram Negative
Aerobes
Growth Temperature = 30°C
Streptococcus



General Information

No information available.

AMZ

Bacterial Identification Result

Sample Information:

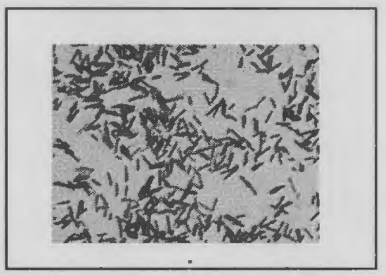
Sample location: Juaymah LANDFARM (Background)
Under the Project No. ARI 660-01-100
Requester: Ramzi Hejazi
Customer ID# 744-640

Result:

Species ID: **VIBRIO VULNIFICUS**

BIOLOG Information

Gram Negative
Aerobes
Growth Temperature = 30°C
Rods.



General Information

FAMILY II. VIBRIONACEAE VERON 1965, 5245

Rigid Gram-negative rods, straight or curved; usually motile by polar flagella but some cells may have, in addition, lateral flagella produced under certain growth conditions. Chemoorganotrophs, metabolism both fermentative and respiratory. Oxidase positive. Several species produce butylene glycol from glucose, some are proteolytic, and some produce indole.

Facultative anaerobes without exacting nutritional requirements. Usually found in fresh or sea water, occasionally in fish or *man.*
The G + C content of the DNA ranges from 39 to about 63 moles %.
Type genus: *Vibrio* Paeini 1854, 411.

Genus Vibrio

(*Pacinia* Trevisan 1885, 83; *Microspira* Schroeter 1886, 168.)

Short asporogenous rods, axis curved, or straight, 0.5 by 1.5—3.0 μm, single or

occasionally united into S shapes *or spirals*. Motile by a single polar flagellum, or, in some species, two or more flagella in one polar tuft; very occasionally non-motile. In some species the flagellum has a central core with an outer sheath (visible in *electron microscope preparations*). Spheroplasts frequently present usually formed in adverse environmental conditions. Gram-negative. Not acid-fast. No capsules. Grow well and rapidly on standard nutrient media.

Chemoorganotrophs, metabolism is both respiratory (oxygen is utilized) and fermentative. Metabolism of carbohydrates is fermentative with mixed products but no CO_2, or H_2. Oxidasepositive. Non-pigmented or yellow. Generally able to grow on simple mineral ammonium media with a simple carbon source; glutamate and succinate are oxidizable substrates, probably universal within the genus, but the range of substrates *utilized* is relatively limited. Frequently V.P. positive. Nitrites usually formed from nitrates. Acid but no gas formed from glucose. Urease negative.

Facultatively anaerobic. Temperature optima *range* from 18—37 C. pH range 6.0—9.0. *Optimum* NaCl requirement usually 3.0% some strains fail to grow in the absence of sodium chloride. Usually sensitive to 2,4-diamino-6,7-diisopropyl pteridine (0/129) and novobiocin.

The G + C content of the DNA (of those species examined) ranges from 40—50 moles %.

Found in fresh and salt water, and in the alimentary canal of man and animals; some species are pathogenic for man and other vertebrates (fish).

Type species: *Vibrio cholerae* Pacini 1854, 411.

Reference: R.E.Buchanan & N.E.Gibbons, 1974, Bergey's Manual of Determinative Bacteriology.

AMZ